CALCULATIONS IN CHEMISTRY

SMITH AND MOORE

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CALCULATIONS OF INORGANIC CHEMISTRY AND QUALITATIVE ANALYSIS

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BY

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PREFACE

This book contains arithmetical problems in inorganic chemistry and qualitative analysis. If qualitative analysis is taught, without any reference to simple physico-chemical relations, the student loses what he learned in inorganic chemistry, and gains only a mechanical knowledge of qualitative analysis. It is desirable, therefore, to continue the applications of physical chemistry, in order that the pupil's knowledge of the principles of chemistry may be still further developed. This book gives only the methods of obtaining the answers by calculation. References to books in which the theory is discussed are given in parenthesis. The references in roman numerals are to pages in Smith's Inorganic Chemistry (3rd Ed., 1917), those in italic numerals are to Smith's College Chemistry (2nd Ed., 1916). References preceded by the letters St. are to Part I of Stieglitz' Qualitative Analysis. The authors will appreciate having any errors called to their attention.

THE AUTHORS.

March 25, 1918.

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CHAPTER I.

UNITS OF MEASUREMENT.

Length. 1 meter (1 m.) = 10 decimeters = 100 centimeters (100 cm.) = 1000 millimeters (1000 mm.).

1 kilometer = 1000 meters (1000 m.).

1 decimeter = 0.1 m. = 10 centimeters = 3.937 inches.

1 meter = 1.094 yards = 3.286 ft. = 39.37 inches.

1 yard = 3 feet = 0.9144 meters.

1 mile = 1760 yards = 1523.98 meters.

1 statute mile = 8 furlongs = 1609.33 meters.

1 sea mile ($\frac{1}{3}$ of a league) = 1854.96 meters.

Volume. 1 liter = 1000 cubic centimeters (1000 c.c.) = a cube 10 cm. × 10 cm. × 10 cm.

1 liter = 0.03532 cu. ft. = 61.03 cu. in. = 1.057 quarts (U. S.) or 1.136 quarts (Brit.) = 34.1 fl. oz. (U. S.) = 35.3 oz. (Brit.).

1 gallon (Brit.) = 4.546 liters; (U. S.) = 3.785 liters.

1 bushel (Brit.) = 36.368 liters; (U. S.) = 35.238 liters.

1 fl. ounce (U. S.) = 29.57 c.c. 1 ounce (Brit.) = 28.4 c.c.

1 cu. ft. = 28.32 liters.

Weight. 1 gram (g.) = wt. of 1 c.c. of water at 4° C. 1 kilogram = 1000 g.

1 gram = 10 decigrams = 100 centigrams (100 cgm.) = 1000 milligrams (1000 mgm.).

1 kilogram = 2.205 lbs. avoird. (U. S. and Brit.).

1 lb. avoird. = 453.6 g.

1 oz. avoird. (U. S. and Brit.) = 28.35 g. 100 g. = 3.5 oz.

1 long ton = 2240 lbs. 1 short ton = 2000 lbs. 1 metric ton = 1000 kilos = 2205 lbs.

1 pound (troy and apoth.) = 12 oz. = 373.24 g.

1 ounce (troy and apoth.) = 31.1035 g.

Temperature. Centigrade: f.-p. water 0°, b.-p. water at 760 mm. 100°. On the Fahrenheit scale, f.-p. water 32°, b.-p. 212°. The same interval is thus 100° on the first scale and 180° on the second. The degree F. is therefore $\frac{100}{180}$ or $\frac{5}{9}$ of 1° C. Conversion formulæ:

$$C.° = \tfrac{5}{9}(F.° - 32). \qquad F.° = \tfrac{9}{5}(C.°) + 32.$$

Pressure. The standard pressure is the average exerted by the atmosphere at the sea level at a latitude of 45°. This is 760 mm. of mercury at 0° = 1 atmos. Since mercury expands when heated, without altering its mass, the height is greater for the same pressure at higher temperatures. Hence the temperature near the barometer must be read, and the height corrected to 0° C. (See Appendix III.)

PROBLEMS.

1. Convert 100 yards into meters. *Ans.* 91.44 m.
2. What is the volume in liters of one cubic yard? *Ans.* 764.64 l.
3. What is the weight in ounces (U. S. and Brit.) of 1000 c.c. of water at 4°? *Ans.* U. S. 33.818, Brit. 35.21.
4. What is the weight in pounds avoird. of 100 g.? *Ans.* 0.2205.
5. What is the weight in grams of five ounces avoird. and apoth.? *Ans.* Avoird. 141.75, apoth. 155.5175.

CHAPTER II.

DENSITIES.

Density. The density of a substance is the weight in grams of 1 cubic centimeter. As all bodies change in volume with change in temperature, the temperature at which the density was measured must also be recorded. Water at 4° C., the temperature at which it has the greatest density, has the density 1. At 4°, 1 c.c. of water weighs almost exactly 1 gram.

Measurement of Density. The density of a solid body is measured by weighing it, and then suspending it by a hair or single thread of silk in water, so that it is completely immersed, and weighing it again. It weighs less in water, by the weight of an equal volume of water. If the water is at 4° C., the density is obtained by dividing the weight of the body by the weight of the equal volume of water:

$$\text{Density } 4° = \frac{\text{Weight of body}}{\text{Wt. of body} - \text{wt. of body in water } (4°)}.$$

Example 1. If a piece of stone weighs 2.52 g. in air and 1.68 in water at 4°, the density = $2.52/(2.52 - 1.68) = 2.52/0.84 = 3$.

In very exact work, the weight of the air displaced must be added to the weight in air.

If the body is weighed in water at some other temperature, say 25°, the weight of the water displaced must be

corrected to 4° (see Appendix I). Thus, in the above example, if the water had been at 25°, the density at 25°

$$= \frac{\text{Weight of body} \times 0.977}{(\text{Wt. of body} - \text{wt. of body in water})}$$
$$= 2.52 \times 0.997/0.84 = 2.46204/0.84 = 2.931.$$

The density of a liquid is determined by weighing a small vessel (pycnometer), first empty, then filled with water at a known temperature, and lastly filled with the liquid. Subtracting the weight of the vessel from the two other weights gives the weights of equal volumes of water and of the liquid at the same temperature.

Example 2. If the vessel weighs 16.523 g. empty, 35.728 g. filled with water at 20°, and 42.786 g. filled with liquid at 20°, the weights of equal volumes of water and of the liquid at 20° are 19.205 g. and 26.263 g. At 4°, the same volume of water weighs $19.205 \times \frac{1.000}{0.998} = 19.243$ g. The density of the liquid at 20° is 26.263/19.243 = 1.365.

The density of a powder, which does not dissolve in water, or interact with water, is determined by weighing a pycnometer, first empty, then filled with water. The powder is also weighed, and is then introduced into the pycnometer, displacing an equal volume of water, and the whole is weighed again.

Example 3. Suppose the weights are: pycnometer empty 16.523 g., with water at 20° 35.728 g., the powder alone 12.651 g., the vessel with water and powder 37.921 g. The volume of the vessel is $(35.728 - 16.523) \times 1.000/0.998 = 19.205/0.998 = 19.243$ c.c. Subtracting the weights of vessel and powder from 37.921, we obtain $37.921 - 16.523 - 12.651 = 8.747$ g. water, which at 4° $= 8.747 \div 0.998 = 8.764$ c.c. Hence 12.651 g. of the powder at 20° occupied $19.243 - 8.764 = 10.479$ c.c. Density at 20° = 12.651/10.479 = 1.207.

PROBLEMS.

6. 1.2562 g. of copper, immersed in water at 20° C., has an apparent weight of 1.1145 g. What is the density of copper? *Ans.* 8.85.

7. The same piece of copper, immersed in carbon disulphide, weighs 1.0767 g. What is the density of carbon disulphide? *Ans.* 1.266.

8. How many grams of aluminium, density 2.670, will displace 125 g. of olive oil, density 0.915? *Ans.* 51.16 g.

9. The density of mercury at 0° is 13.596; at 20° it is 13.558. Neglecting the expansion of the iron, what weight of mercury will be extruded if an iron pipe holding 12,600 c.c., full of mercury at 0°, be heated to 20° C.? *Ans.* 4783.2 g.

10. One variety of sulphur has a specific gravity of 2.06; there is a second variety having a density of 1.96. A certain weight of sulphur was changed from the first to the second variety and in changing expanded 1.246 c.c. What is the weight of this mass of sulphur? *Ans.* 49.84 g.

11. A certain solid having a density of 0.875 is made into a cube having an edge 5 cm. long. This solid is floated on water at 4° C. What is the area of the portion exposed above water? *Ans.* 37.5 sq. cm.

12. A rectangular solid $2 \times 3 \times 4$ cm. weighs 39.60 g. It is soaked in water and then weighed in water. Its weight in water is 19.39 g. Calculate its apparent density, its real density and its porosity. *Ans.* 1.65; 1.96; 18.79 per cent.

13. What are the relative weights of an aluminium and a copper wire of equal length whose cross sections are so chosen that they have the same electrical resistance? Resistance per centimeter cube of aluminium is 0.30×10^{-5} ohms; of copper 0.17×10^{-5} ohms. Density of aluminium 2.70, of copper 8.9. *Ans.* Copper 1.87 times heavier than aluminium.

14. If the coefficient of linear expansion of zinc is 0.000029, what will be the density of unpressed zinc at 30° C. if its density at *20° C.* is *6.923* (referred to water at 4° in each case)? *Ans.* 6.917.

15. The coefficient of cubical expansion of ethyl alcohol is 0.00110; of water is 0.00018. The density of alcohol at 20° is 0.789; of water at 20° is 0.998. What is their relative density at 70° C.? *Ans.* 1.323.

16. A glass tube is immersed in a beaker of water at 40° C. The air is exhausted through the open end of the tube until the water has risen 18 cm. If a second tube were immersed in olive oil at 4° C. and exhausted simultaneously by the *same* pump, how far would it rise above the surface of the oil in the beaker, neglecting the capillary rise in each tube? (Density of olive oil = 0.915.) *Ans.* 19.67 cm.

How would you suggest avoiding the capillary correction, experimentally?

17. If the diameter of the two tubes in problem **16** are 8 and 17 mm., respectively, what will be the weights of water and oil in the tubes? *Ans.* 9.048 g.; 40.855 g.

18. A rectangular solid of density 0.85, having dimensions $8 \times 5 \times 3$ cm., is floating on water, with the largest surface on the water. What weight must be added to it to make the upper surface lie in the same plane as the surface of the water? *Ans.* 18 g.

19. A pycnometer, filled with water at 25° C., weighs 41.814 g. Filled with a certain oil, it weighs 42.735 g. Empty, the pycnometer weighs 17.643 g. What is the density of the oil referred to water at 4° C.? *Ans.* 1.0412.

20. Calculate the density of cadmium from the following data:

Pycnometer, empty, weighs 17.643 g.

Pycnometer, full of water, 25°, weighs 41.814.

Pycnometer, containing 10.000 g. cadmium and filled to top with water at 25°, weighs 50.659 g. *Ans.* 8.633.

21. If 10 g. ordinary tin (density = 7.28) had been used in **20** what would the pycnometer, water and tin have weighed? *Ans.* 50.441.

22. A cylindrical vessel is graduated in tenths of a cubic centimeter, the zero being at bottom. It contains water at 18° C. up to the 50.0 c.c. mark. 25.47 g. of quartz (density = 2.648) is now put into this vessel. What is the reading of the water level? *Ans.* 59.62 c.c.

CHAPTER III.

LAWS OF GASES.

The volume of a gas changes with change in pressure. The volume, or the pressure, changes also with change in temperature.

Boyle's Law. At constant temperature, the concentration of a gas is proportional to the pressure. The volumes occupied by a sample of any gas are inversely proportional to the pressure at each volume [103–108, *70–72*].

Example 4. If the volume of a gas is 250 c.c. at 735 mm., what will be its volume at 760 mm. pressure? The new pressure is greater, therefore the new volume will be less. Hence $250 \times \frac{735}{760} = 241.8$ c.c. at 760 mm. Since the new volume is to be *less*, the *smaller pressure* is placed in the numerator.

Charles' Law. When the pressure is kept constant, the volume changes in proportion to the absolute temperature. The absolute temperatures are obtained by adding 273° to the temperatures centigrade [108–110, *72*].

Example 5. If a gas occupies 350 c.c. at 18° C., what volume will it occupy at 0° C? Adding 273°, the temperatures become 291° Abs. and 273° Abs. As 273° is lower than 291°, the new volume will be less. Hence $350 \times \frac{273}{291} = 328.3$ c.c., volume at 0° C.

Example 6. Again, if a gas occupies 400 c.c. at 20° C., what volume will it occupy at −10° C.? Add 273° *algebraically:* 293° Abs. and 263° Abs. $400 \times \frac{263}{293} = 359$ c.c. at −10° C.

Correction for Water Vapor. If the gas is measured over water, the vapor pressure of the water (Appendix II) must be subtracted from the barometric reading, the difference being the pressure of the gas. Thus 30 c.c. of gas over water at 752 mm. pressure and 15° includes 12.7 mm. pressure of water vapor. The difference 752 − 12.7 = 739.3 mm. is the pressure of the gas alone. The last value is the one used in calculations [111, *72*].

Example 7. 198 c.c. of gas is at 751 mm. and 11° over water. What will be its pressure when the volume is 190 c.c. and the temperature is 20°, and the gas is dry? 751 mm. − 9.8 mm. = 741.2.

$$198 \times \frac{293}{284} \times \frac{741.2}{x} = 190$$

$$x = \frac{198}{190} \times \frac{293}{284} \times 741.2 = 802.6 \text{ mm.}$$

Humidity. Humidity of air, or any gas, is the ratio of the partial pressure of the water vapor present to that required for saturation. The partial pressure is measured by finding the dew-point. Thus, if air at 18° C. has to be cooled to 11° C. before it deposits dew, it contains water vapor at a pressure of 9.8 mm. (Appendix II). If saturated at 18°, the partial pressure of water vapor would have been 15.4 mm. The relative humidity was, therefore, 9.8/15.4 or 63.6 per cent [502, *330*].

PROBLEMS.

23. 200 c.c. of hydrogen are measured at 736.4 mm. and 28° C. What is its volume under standard conditions? *Ans.* 171.76 c.c.

24. 150 c.c. of a gas shows a pressure of 732 mm. at −10°. What will be its volume at 18° and 752 mm. *Ans.* 161.66 c.c.

25. 175 c.c. of a gas is at 745 mm. and 7°. What will be its pressure when the volume is 170 c.c. and the temperature 18°? *Ans.* 797 mm.

26. A liter of air weighs under standard conditions 1.293 g.; a liter of hydrogen weighs under the same conditions 0.0899 g. What weight will a balloon, filled with hydrogen, sustain, if its capacity is 15 cubic meters, and the pressure and atmospheric temperature are respectively 728 mm. and 20° C.? *Ans.* 15.739 kg.

27. To what pressure must a body of argon be subjected, in order that its temperature may be 20° C. and its volume 157.4 c.c., when its volume at 14° C. and 753 mm. is 208.4 c.c.? *Ans.* 1027.8 mm.

28. A body of nitrogen is measured as 125 c.c. over water at 754 mm. barometric pressure and at a temperature of 12° C. What volume would the dry nitrogen occupy at 780 mm. and 22° C.? *Ans.* 123.3 c.c.

29. A certain space having a volume of 150 c.c. is filled with saturated water vapor at a temperature of 25° C. Into this space is admitted hydrogen at the same temperature, until the pressure is equal to the external atmospheric pressure. The hydrogen admitted had a volume of 183 c.c. under a pressure of 740 mm. and at 30° C. What is the external atmospheric pressure? *Ans.* 766.15 mm.

30. 128.4 c.c. of oxygen is measured over water, at 20° C. and a pressure of 764.7 mm. It is then mixed with 477.8 c.c. of dry nitrogen, measured at a temperature of 13° C. and 742 mm. pressure. The mixture is now compressed until it has a volume of 508 c.c. at 17° C. What pressure is required? *Ans.* 915.1 mm.

31. In **30** calculate the partial pressures of oxygen, nitrogen and water vapor, and the degree of humidity of the mixture. *Ans.* 0.246 atmos., 0.952 atmos., 0.006 atmos., 31.4 per cent.

32. A mixture of nitrogen and hydrogen is made. The total volume is 743 c.c. at 10° C. and 758.7 mm. The volume of the hydrogen at 22° C. and 746.4 mm. was 421.66 c.c. What was the volume occupied by the nitrogen at a temperature of 19° C. and 766 mm. pressure? *Ans.* 352.7 c.c.

33. The mixture in **32** is saturated with water vapor. What is the total pressure now? *Ans.* 767.9 mm. It is now compressed until the pressure is 780 mm. and then cooled to 7° C. What are the partial pressures of each constituent? *Ans.* H_2O 0.009 atmos., H_2 0.545 atmos., N_2 0.472 atmos.

34. What is the volume at 749 mm. and 24° C. of 843 c.c. of chlorine, measured at 764 mm. and 32° C.? *Ans.* 837 c.c.

35. What pressure is required to compress 760 c.c. of carbon monoxide, measured at 753 mm. over water at 18° C., to 712 c.c. at 27° C. over water? *Ans.* 838.2 mm.

36. 65.55 g. of sulphur dioxide occupy 22.4 l. under standard conditions. What weight of this gas would occupy this volume at 10° C. and 743 mm. pressure? *Ans.* 61.82 g.

37. What is the relative density of sulphur dioxide compared to O_2 in the above two cases, if 1 l. oxygen under standard conditions weighs 1.429 g.? *Ans.* 2.05 : 1; 1.93 : 1.

38. 22.4 l. of carbon dioxide weigh 41.89 g. at 10° C. and under 750 mm. pressure. What is the weight of this volume of CO_2 under standard conditions? *Ans.* 44.00 g.

39. 24 g. of carbon dioxide and 73 g. of sulphur dioxide are mixed. The volume of the mixture is 32.45 l. and the temperature is 18° C. What is the partial pressure of each gas? (Use data from **37** and **38.**) *Ans.* CO_2 305.03 mm.; SO_2 622.8 mm.

40. Two bulbs of equal capacity (100 c.c.), connected by a capillary, are filled with nitrogen at a pressure of 720 mm., at 20° C. Assuming no change in volume, what is the pressure within the system if both bulbs are heated to 250° C.? *Ans.* 1285 mm.

41. What is the relative density of the gas in the bulbs, respectively, in **40**? *Ans.* Same; 0.0011 g. per 1 c.c.

42. Dry air, free from carbon dioxide, contains by volume 78.06 per cent of nitrogen, 21 per cent oxygen and 0.94 per cent argon. What is the partial pressure of each of these constituents at 760 mm. pressure? *Ans.* N_2 593.256 mm.; O_2 159.6 mm.; A 7.144 mm.

43. What is the weight of the atmospheric oxygen in a room $3 \times 4 \times 6$ meters, if the air is at 18° C. and 733 mm. pressure, the air having the composition of **42** above? *Ans.* 84,234 g.

44. If 2 g. of carbon dioxide are introduced into a bottle of 2500 c.c. capacity holding air from the room in **43** above, and none of the gases are allowed to escape, calculate total pressure. *Ans.* 1062.82 mm.

45. If the carbon dioxide in **44** displaced its own volume of air, the pressure remaining constant, calculate the partial pressure of each constituent. *Ans.* N_2 314.72 mm.; O_2 84.67 mm.; A 3.79 mm.; CO_2 329.82 mm.

CHAPTER IV.

CALCULATION OF FORMULÆ, AND CALCULATIONS FROM EQUATIONS.

Making Formulæ. To make the formula of a compound substance, assuming the formula to be unknown, two kinds of information are required. We ascertain (1) **by measurement** the proportion by weight of the constituents in the compound. We require also (2) to know the chemical unit weights — the atomic weights — which have been accepted by chemists for each constituent element. By factoring the terms of the first proportion so that one factor in each case is the atomic weight, we discover whether multiples of the atomic weights will be required to represent the composition of the substance, and if so what these must be.

Example 8. Suppose the problem is to make the formula of dried rust. By weighing before and after the change, we get the weight of the iron and of the corresponding amount of oxygen in the rust it produces. If we took 2 g. of iron we should get about 2.86 g. of rust. So that the proportion of iron to oxygen is $\frac{2}{0.86}$. Now, in the formula, the same ratio must be represented by means of multiples of the atomic weights. We therefore divide the quantity of each element by the corresponding atomic weight. This gives us the factors by which the atomic weights are to be multiplied. The atomic weights are 55.8 and 16, respectively: $2 \div 55.8 = 0.0358$, and

$0.86 \div 16 = 0.0537$. The proportion $\frac{2}{0.86}$ then becomes $\frac{55.8 \times 0.0358}{16.0 \times 0.0537}$. Now this proportion must be capable of expression in terms of *integral* multiples of the atomic weights. We find that the greatest common measure of the two factors is 0.0179. Dividing above and below by this, we obtain the ratio $\frac{55.8 \times 2}{16.0 \times 3}$. Substituting the symbols for the atomic weights, the proportion appears as $\frac{Fe \times 2}{O \times 3}$, and the formula is therefore Fe_2O_3.

Example 9. Applying the same process to cupric oxide, we start with the result of the measurement: copper : oxygen : : 85 : 21.

$$\frac{\text{Copper}}{\text{Oxygen}} = \frac{85}{21} = \frac{63.57 \times 1.3}{16 \times 1.3} = \frac{Cu \times 1.3}{O \times 1.3} = \frac{Cu}{O} \text{ or } CuO.$$

Example 10. If the composition of the substance has been stated in percentages, the same device is used. Thus, the case of sodium sulphate works out as follows:

Elements.	Percentages.	At. Wt. Quotient ÷		Formula
Sodium.....	32.43	23 × 1.41	0.705	Na × 2
Sulphur.....	22.55	32 × 0.705	0.705	S
Oxygen.....	45.02	16 × 2.814	0.705	O × 4

The formula is, therefore, Na_2SO_4.

It is obvious that, after we have found out what elements compose a given compound, we are still unable to write its formula. We may *not* simply set the symbols down, side by side. A measurement must be made, in order that we may find out the factors by which the atomic weights are to be multiplied.

Calculations from Formulæ and Equations. As we have seen (p. 12), the formula represents the composition of a substance, using the atomic weights as the units. We have learned how the formula is calculated from measurements made in an experiment (p. 12). We may now take up some of the ways of using the information contained in a formula.

Example 11. Composition from the Formula. Formula-Weight. To learn the composition of a substance, such as potassium chlorate $KClO_3$, from its formula, we look up the values of the atomic weights (Appendix IV). We find K = 39.1 parts of potassium, Cl = 35.46 parts of chlorine, and $O_3 = 3 \times 16$ or 48 parts of oxygen. The proportions, in order, are therefore: 39.1 : 35.46 : 48.

What is the proportion of oxygen to potassium and chlorine, together? It is 48 : 39.1 + 35.46, or 48 : 74.56, or 1 : 1.55.

We require a name for the sum of the weights of the constituents indicated in the formula. This is called the **formula-weight.** Thus, for potassium chlorate, it is 39.1 + 35.46 + 48, or 122.56.

Example 12. To Find the Percentage Composition. In potassium chlorate the proportions are 39.1 of potassium, 35.46 of chlorine, and 48 of oxygen or a total of 122.56. In one hundred parts, the potassium is $\frac{39.1}{122.56} \times 100$, or 31.9; the chlorine $\frac{35.46}{122.56} \times 100$, or 28.9; and the oxygen $\frac{48}{122.56} \times 100$, or 39.1.

Stated in terms of the rule of proportion, we have, for the potassium, 122.56 : 39.1 : : 100 : x, where x is the percentage of potassium.

Calculations by Use of Equations. We frequently wish to know what weight of a product can be obtained from a given weight of the necessary materials, or how much material is required to furnish the desired weight of a product. For example, what weight of ferrous sulphide can be made with 100 g. of iron? It is understood that the necessary sulphur is available.

Example 13. To avoid the blunders which are easily made, observe strictly the following rules:

1. **Write down the equation:**

$$Fe + S \rightarrow FeS.$$

2. **Place under each formula the weight it represents:**

$$\begin{array}{ccccc} Fe & + & S & \rightarrow & FeS. \\ 55.84 & & 32.06 & & 87.9 \end{array}$$

3. **Read this expanded equation.** In this case it reads: 55.84 parts of iron combine with 32.06 parts of sulphur to give 87.9 parts of ferrous sulphide.

4. **Re-read the original problem:** "What weight of ferrous sulphide can be made with 100 g. of iron?" Having done this, place the amount given in the problem (100 g. of iron) under the formula of the substance in question. Then notice what the problem asks ("what weight of ferrous sulphide") and place an x under the formula of that substance:

$$\begin{array}{ccccc} Fe & + & S & \rightarrow & FeS. \\ 55.84 & & 32.06 & & 87.9 \\ 100\ g. & & & & x \end{array}$$

5. **Read the problem as now tabulated:** 55.84 g. of iron give 87.9 g. of ferrous sulphide, therefore 100 g. of iron will give x g. of ferrous sulphide.

6. **State the proportion in this order** (or, see below).

$$55.84 : 87.9 : : 100 : x \ (= 157.5 \text{ g.}).$$

If the tabulation in rule 4 has been prepared correctly, this final statement as a proportion is purely mechanical. It will be noted that only two of the three quantities given in the expanded equation were actually used.

6a. **Alternative method.** At the sixth step, we may also say: If 55.84 g. of iron give 87.9 g. of ferrous sulphide, 1 g. of iron will give $\frac{87.9}{55.84}$ g. (= 1.575 g.) of ferrous sulphide. Then, if 1 g. of iron gives 1.575 g. of ferrous sulphide, the 100 g. of iron will give 100×1.575 g. (= 157.5 g.) of ferrous sulphide.

Warnings. In solving the problems beware of three kinds of mistakes, which are commonly made.

1. Do not read the problem carelessly and make the equation backwards, that is, with the sides reversed. Focus attention first on the exact chemical change involved.

2. Do *not* speak, or think of the symbols Fe and S as standing for "1 part" of iron or sulphur. They stand for 1 *chemical unit,* or atomic weight, or atom, in each case, that is, for "55.84 parts" and "32.06 parts," respectively.

3. Follow the rules laid down above. The chemist follows these rules. The beginner always thinks he can do without them, and he fails in consequence. Writing the equation in expanded form (rule 2) and reading the problem into it (rules 4 and 5) are absolutely essential steps.

Example 14. What weight of hydrogen is required to reduce 45 g. of magnetic oxide of iron to metallic iron?

Following the rules, as before, we reach the expanded equation:

Fe_3O_4	+	$4H_2$	→	3Fe	+	$4H_2O$.
$3 \times 55.84 + 4 \times 16$		8×1.008		3×55.84		$4(2 \times 1.008 + 16)$
$167.52 + 64$		8.064		167.52		4×18.016
231.52		8.064		167.52		72.064
45 g.		x				

Observe that the atomic weights are multiplied by the sub-numbers, so that, for example, $Fe_3 = 3 \times 55.84$. Observe also that the formula-weights are multiplied by the coefficients, when such occur, in front of the formulæ, so that, for example, $4H_2O = 4 \times 18.016$.

The proportion $231.52 : 8.064 :: 45 : x$ $(= 1.57)$ supplies the answer, 1.57 grams of hydrogen.

Using the alternative plan: If 231.52 g. of magnetic oxide are reduced by 8.064 g. of hydrogen, 1 g. will be reduced by $\frac{8.064}{231.52}$ g. $(= 0.035$ g.) of hydrogen. Hence, if 1 g. of magnetic oxide is reduced by 0.035 g. of hydrogen, 45 g. will be reduced by 45×0.035 g. $(= 1.57$ g.) of hydrogen.

Equivalent Weights. The equivalent weight of an element is that weight which will combine with, or displace, 1.008 g. of hydrogen, 8 g. of oxygen, or 35.46 g. of chlorine [63, *65*].

PROBLEMS.

46. If 26 g. of mercurous oxide are required to give, by heating, 1 g. of oxygen, what is the formula of the substance? *Ans.* Hg_2O.

47. What are the formulæ of the substances possessing the following percentage compositions?

I	II	III
Magnesium, 25.57	Sodium, 32.43	Potassium, 26.585
Chlorine, 74.43	Sulphur, 22.55	Chromium, 35.390
	Oxygen, 45.02	Oxygen, 38.025
Ans. $MgCl_2$	Na_2SO_4	$K_2Cr_2O_7$.

48. What are the percentage compositions of hausmannite Mn_3O_4, potassium bromide KBr, ferrous sulphate $FeSO_4$? *Ans.* Mn 72.03, O 27.97; K 32.85, Br 67.15; Fe 36.76, S 21.1, O 42.13.

49. What weight of hydrogen is required to reduce 100 g. of ferric chloride $FeCl_3$ to ferrous chloride $FeCl_2$ (hydrogen chloride HCl is formed)? *Ans.* 0.62 g.

50. Calculate the formula of the oxide of tin formed when 2 g. of tin give 2.54 g. of the oxide. *Ans.* SnO_2.

51. What weight of oxygen can be obtained by heating 8 g. of mercuric oxide? *Ans.* 0.59 g.

52. An excess of hydrogen is mixed with the oxygen set free in **51** and exploded. How much water is formed? *Ans.* 0.66 g.

53. How much zinc would be required to set free, from hydrochloric acid, the hydrogen used in **52**? *Ans.* 2.29 g.

54. How much carbon dioxide is formed by the combustion of 10 g. benzene C_6H_6? *Ans.* 33.2 g.

55. How much water is formed in **54**? *Ans.* 6.92 g.

56. An excess of chlorine is allowed to act on 18 g. phosphorus. How much phosphorus pentachloride is formed? *Ans.* 121.06 g.

57. What weight of silver chloride is precipitated when a solution containing 2.54 g. of potassium chloride is mixed with an excess of silver nitrate? *Ans.* 4.88 g.

58. How much nitrogen is there in 10 g. of ammonia? *Ans.* 8.23 g.

59. How much sodium nitrate is formed when a solution containing 15 g. of sodium hydroxide is neutralized with nitric acid and evaporated to dryness? *Ans.* 31.88 g.

60. When anilin $C_6H_5NH_2$ is burned in a stream of oxygen, and the products of combustion are passed over hot copper, nitrogen is set free. How much nitrogen would be obtained if 0.4321 g. of anilin are burned? *Ans.* 0.065 g.

61. Under certain conditions nitric acid can be reduced to ammonia. Expressed in the simplest term, the reaction is: $HNO_3 + 8H \rightarrow 3H_2O + NH_3$. How much ammonia is obtained if 2.57 g. nitric acid be reduced? *Ans.* 0.694 g.

62. If 14.34 g. of hydrogen bromide are oxidized by manganese dioxide, how much bromine is set free? *Ans.* 7.08 g.

63. 10 g. of iodine are suspended in water and hydrogen sulphide passed in. How much sulphur is formed? *Ans.* 1.26 g.

64. How much sulphuric acid contains the amount of sulphur formed in **63**? *Ans.* 3.86 g.

65. What weight of barium sulphate is formed if the sulphuric acid of **64** is mixed with barium chloride solution? *Ans.* 9.18 g.

66. 10 g. of calcium oxalate CaC_2O_4 are heated until converted into calcium oxide. What weight of CaO is formed? *Ans.* 4.37 g.

67. What weight of magnesium sulphate, $MgSO_4,7H_2O$, is required to give a precipitate of magnesium-ammonium phosphate $MgNH_4PO_4,6H_2O$ weighing 3.47 g.? *Ans.* 3.48 g.

68. What weight of zinc oxide is obtained when 100 kilos of zinc-blende ZnS, 84 per cent pure, is roasted? *Ans.* 70.2 kg.

69. How much mercuric sulphide HgS is precipitated when 47.4 c.c. of a 2 per cent solution of mercuric chloride is saturated with hydrogen sulphide? *Ans.* 0.812 g.

70. What weight of cadmium hydroxide is required to make 125 c.c. of 5 per cent cadmium chloride solution? *Ans.* 4.99 g.

71. How much fluorine is in 10 g. of cryolite Na_3AlF_6? *Ans.* 5.43 g.

72. How much potassium permanganate is required to oxidize 0.456 g. of ferrous sulphate to ferric sulphate? *Ans.* 0.0948 g.

73. How much silver is contained in 100 g. of an impure specimen of silver chloride which is 33 per cent sand? *Ans.* 57.9 g.

74. What are the equivalent weights of aluminium in aluminium chloride $AlCl_3$, of iron in ferric chloride $FeCl_3$ and in ferrous sulphate $FeSO_4$, and of tin in stannous oxide SnO and in stannic oxide SnO_2? Al 9.03; Fe 18.91, 27.92; Sn 59.3, 29.67.

75. Silver oxide contains 93.09 per cent of silver. If we assume the equivalent weight of oxygen is 8, calculate the equivalent weight of silver. *Ans.* 107.77.

76. In an actual experiment 10.1435 g. of silver combined with bromine and formed 17.6577 g. of silver bromide. How many grams of bromine would combine with 107.88 g. of silver? (J. Am. Chem. Soc., **37** (1915), 95.) *Ans.* 79.92.

77. Calculate the percentage composition of silver bromide from the above figures. *Ans.* Br 42.55 per cent; Ag 57.45 per cent.

78. In cadmium chloride the ratio Cd : Cl_2 is 1.5853 : 1. If we start with 121.38 g. of metallic cadmium, how many grams of cadmium chloride can we get? (J. Am. Chem. Soc., **37** (1915), 113.) *Ans.* 192.42.

79. 5.03774 g. of silver replaced the iron in 5.03555 g. of ferrous bromide, forming 8.76950 g. of silver bromide. If the equivalent wt. of silver is 107.88, what is the equivalent wt. of iron? (Baxter et al., J. Am. Chem. Soc., **33** (1911), 332.) *Ans.* 27.92.

80. From the values given for silver and silver bromide in **76,** above, we have deduced the equivalent weight of bromine. We may denote this quantity by the symbol Br. From 10.1859 g. of calcium bromide there was obtained 19.1378 g. of silver bromide. Using the equivalent weights of silver and bromine in **76** calculate the equivalent weight of calcium (Richards and Hoenigschmid, J. Am. Chem. Soc., **32** (1910), 1577). *Ans.* 20.04.

81. Calculate the percentage composition of ferrous bromide from the data in **79.** *Ans.* Fe 24.96, Br 75.04.

82. Mercuric chloride contains 73.883 per cent of mercury, and 26.118 per cent of chlorine. 10.50276 g. of mercuric chloride contain enough chlorine to form 11.08744 g. of silver chloride. Using 107.88 as the equivalent weight of silver, calculate the equivalent weight of mercury. (Easley, J. Am. Chem. Soc., **31** (1909), 1207; **32** (1910), 1117.) *Ans.* 100.31.

83. From the data above calculate the percentage composition of silver chloride. *Ans.* Ag 75.26, Cl 24.74.

84. There is another compound of mercury and chlorine, containing 84.94 per cent of mercury. Using the equivalent weight of mercury obtained above in **82,** calculate the equivalent weight of chlorine and compare with the accepted equivalent weight 35.46. Adjust the discrepancy. *Ans.* 17.78, for 200.62 of mercury 35.56.

85. If we take 200.00 as the atomic weight of mercury, and 35.46 as that of chlorine, calculate the formulæ of the two chlorides above mentioned. *Ans.* $HgCl_2$, HgCl.

86. Using the equivalent weight of iron calculated in **79** and that of chlorine given in **84,** calculate the percentage composition of *one* of the chlorides of iron. *Ans.* Fe 44.05, Cl 55.95.

87. Pure ferric oxide contains 69.94 per cent of iron. Assuming the equivalent of oxygen is 8, calculate the equivalent weight of iron. Compare with the result obtained in **79.** (Baxter & Hoover, J. Am. Chem. Soc., **34** (1910), 1657.) *Ans.* 18.61.

88. Find the least common multiple of the two equivalents of iron, found in **79** and **87.** What name is given to this value? Denote this quantity by Fe. *Ans.* 55.84 at. wt. of iron.

89. From the results of **88, 87, 79** and **80,** write the formulæ of the two bromides of iron. What is the ratio, bromine to bromine, in the two compounds? *Ans.* $FeBr_2$, $FeBr_3$; 16 : 24.

90. From the result in **87,** and the accepted equivalent for chlorine 35.46, calculate the percentage composition of the *other* chloride of iron. *Ans.* Fe 34.42, Cl 65.58.

91. Using any arbitrary amount of iron and the results of **86** and **90,** calculate the amounts of chlorine with which this amount of iron will combine to form the two chlorides of iron. What is the chlorine : chlorine ratio in these two compounds? *Ans.* 10 g. Fe; 12.70, 19.05 Cl; 2 : 3.

92. Write the formulæ of the two chlorides of iron, using the method outlined in **89.** *Ans.* $FeCl_2$, $FeCl_3$.

93. 1.283 g. of sodium set free, from water, 680.41 c.c. of hydrogen, measured at 20° C. and 758 mm. pressure (over water). What is the equivalent of sodium? *Ans.* 23.11.

94. An oxide of sulphur contains 50 per cent of sulphur and 50 per cent of oxygen. A second oxide of sulphur, 60 per cent oxygen and 40 per cent sulphur. Calculate the equivalent weights of sulphur. *Ans.* 8, 5.33.

95. 7.84 g. of zinc is immersed in an acidulated copper sulphate solution, and the action allowed to proceed until all the zinc is dissolved. If 2 per cent of the zinc is used in setting hydrogen free and 98 per cent in setting copper free, what volume of hydrogen, collected over water at 19° C. and at a barometric pressure of 756 mm., is liberated; what weight of copper will be formed? *Ans.* H_2 584.5 c.c.; Cu 7.44 g.

96. A sample (100 g.) of iron pyrites contains 94.77 per cent FeS_2. What volume of sulphur dioxide, measured at 30° C. and 729 mm. pressure, is formed if this material be completely oxidized and the product of combustion contains 0.23 per cent sulphur trioxide? *Ans.* 40.81 l.

97. A solution is made by diluting with water 14.33 c.c. of 94.68 per cent sulphuric acid until the volume is 186.41 c.c. When the mixture has resumed the original temperature of the component solutions, 74.66 c.c. of this mixture is mixed with 10 c.c. of a solution of barium chloride containing 17.46 g. of the salt in 134 c.c. What weight of barium sulphate is precipitated, assuming the reaction to be a complete one? (Hint: Look up the specific gravity of the sulphuric acid.) *Ans.* 1.243 g.

1.460

98. Which of the factors in **97** above are in excess? If 2.26 g. of the substance not in excess be added, what further weight of barium sulphate will be thrown down? *Ans.* H_2SO_4, 2.159 g.

99. Calculate the percentage composition of the following compounds: $KAl(SO_4)_2,12H_2O$; H_2PtCl_6; $CeCl_3$; $CaCl_2,6H_2O$; $K_2S_2O_7$; CaB_4O_7; Na_2HgI_4; $NaNH_2$; NH_4OCN; $K_3Co(CN)_6$. *Ans.* K 8.24, Al 5.71, S 13.51, O 67.44, H 5.1; H 0.49, Pt 47.61, Cl 51.89; Ce 56.86, Cl 43.13; Ca 18.30, Cl 32.37, H 5.52, O 43.81; K 30.75, S 25.21, O 44.04; Ca 20.43, B 22.44, O 57.12; Na 6.10, Hg 26.61, I 67.30; Na 58.94, N 35.9, H 5.15; N 46.65, H 6.71, O 26.64, C 19.99; K 35.29, Co 17.74, C 21.67, N 25.29.

100. What weight of strontium phosphate contains the same amount of phosphorus as 165.4 g. phosphonium iodide? *Ans.* 231.25 g.

101. A sample of magnesium carbonate is 93.46 per cent pure, the impurity being silica. 47.85 g. of this material is heated for a few moments and the carbon dioxide evolved caught over mercury and measured. It occupied 3.78 liters at 743.17 mm. and 21° C. Calculate the percentage composition of the residue. *Ans.* SiO_2 7.61, $MgCO_3$ 77.34, MgO 15.05.

102. A sample of lithium chloride has absorbed moisture up to 32.05 per cent of its original weight. What was the original weight, if the sample, dissolved in water, yields 4.276 g. of silver chloride on the addition of a little nitric acid and an excess of silver nitrate? *Ans.* 1.26 g.

103. What weight of sylvite, containing 96.48 per cent potassium chloride, contains the same weight of chlorine as 14.76 g. of a solution made by dissolving 28.96 g. of pure sodium chloride in 172.41 g. of water? *Ans.* 2.229 g.

104. What weight of water would be expelled from 10.472 g. of hydrated barium chloride ($BaCl_2,2H_2O$) on heating? *Ans.* 1.544 g.

105. How many grams of calcium chloride $CaCl_2,6H_2O$ would contain the water expelled in **104**? *Ans.* 3.129 g.

106. What weight of calcium chloride $CaCl_2,6H_2O$ would be chemically equivalent to the $BaCl_2,2H_2O$ in **104**? *Ans.* 9.212 g.

107. What weight of boric oxide contains the same amount of boron as 143.84 g. of boron nitride? *Ans.* 201.37 g.

108. How many grams of cerium dioxide contain the same weight of oxygen as 66.43 g. of zinc oxide? *Ans.* 70.30 g.

109. The percentage of iron in a mixture of ferric oxide and magnetite is 71.38. What is the molar ratio of the two components? *Ans.* $Fe_2O_3 : Fe_3O_4 :: 1 : 1.016$.

110. What volume of hydrogen measured at 738.66 mm. and 130° C. would be formed if the magnetite in 18.46 g. of the above mixture had been obtained by blowing steam over red hot iron? *Ans.* 7.559 liters.

111. What weight of iron would be required to yield this quantity of magnetite? *Ans.* 9.303 g.

112. 124.66 g. of lead acetate (look up the formula of the crystallized salt) are contained in 1544.7 c.c. of its solution. 174.48 c.c. are taken and the lead precipitated by means of zinc. How much lead is obtained? *Ans.* 7.692 g.

113. The remainder of the solution in **112** is treated with sodium hydroxide and then with chlorine until 74.66 per cent of the theoretically possible amount of lead dioxide is precipitated. How much lead dioxide is formed? *Ans.* 52.07 g.

114. How much potassium chlorostannate K_2SnCl_6 contains the same weight of tin as 14.37 g. of tin dioxide? *Ans.* 39.06 g.

115. Calculate the percentage composition of: Carborundum, calcium carbide, silico-methane, silicon oxychloride Si_2OCl_6, tin tetrachloride, iodoform. *Ans.* Si 70.22, C 29.77; Ca 62.53, C 37.47; Si 87.61, H 12.38; Si 19.83, O 5.61, Cl 74.56; Sn 45.56, Cl 54.44; C 3.05, I 96.69, H 0.26.

116. How much silicon in 41.27 g. of a sample of calcium metasilicate, if the mineral (wollastonite) is 96.44 per cent pure, 2.42 per cent being silicon dioxide? *Ans.* 10.15 g.

117. How many grams of magnesium pyrophosphate are left when a precipitate of magnesium-ammonium phosphate (look up formula), weighing 0.8647 g., is ignited? *Ans.* 0.7848 g.

118. 5.00 grams each of the following salts are taken: If it were possible to get the total nitrogen from all these salts, as free nitrogen, what volume would it occupy at 744.71 mm. and 20° C. (collected over water): KNO_3; $Hg(NO_3)_2$, $8H_2O$; $Pb(NO_3)_2$; $AgNO_3$? *Ans.* 621.75 c.c.; 268.8 c.c.; 379.59 c.c.; 361.33 c.c.

119. What weight of nitric acid (68 per cent acid by weight) would contain the same amount of nitrogen as 5 g. of KNO_3 (**118**)? *Ans.* 4.60 g.

120. A merchant buys 800 short tons of sodium sulphate deca-

hydrate at 55¢ (2/3½) per hundredweight. During storage, it becomes Na_2SO_4,H_2O. The merchant had planned to make a profit of $1400 (£288 13*s.* 3*d.*) on the lot. For what price per short ton must he sell this effloresced material to make this profit? *Ans.* $25.66 (£5 5*s.* 5*d.*).

121. Which is the cheaper source of 8000 lbs. of potassium chloride: Potassium hydroxide at 8¢ (4*d.*) per lb. or potassium carbonate at 6¢ (3*d.*) per lb., the carbonate being 85 per cent pure and the hydroxide containing 17 per cent carbonate? Give difference in cost, assuming labor and other charges the same in the two instances. *Ans.* KOH $26.04 (£5 7*s.*) less.

122. What will be the profits on 1000 tons of phosphorus sold at 80¢ (3/4) per lb., if the raw material is (*a*) Florida phosphate rock at $2.50 (10/5) per ton and (*b*) Tenn. phosphate at $5.50 (23/3) per ton, the Florida rock containing 68 per cent calcium phosphate, the Tennessee rock containing 80 per cent; the recovery in the first case being 84 per cent of the phosphorus and 91 per cent in the latter, the freight and labor charges, etc., being estimated at 30 per cent of the selling cost of the phosphorus? *Ans.* (*a*) $901,240 (£185,059 10*s.*); (*b*) $724,590 (£148,786 8*s.*).

123. How many lbs. of calcium tungstate, which is 83.85 per cent pure, are required to make enough tungsten for 1,000,000 lamps, each containing a filament 50 cm. long and 0.0039 cm. in diameter? (Assume 98 per cent recovery of W.) Density of W 19.5. *Ans.* 49.035 lbs.

124. An electric furnace is heated by 10 resistors, each of which weighs 176 g. and is made of 45 per cent nickel and 55 per cent chromium. How much chromite ($Fe(CrO_2)_2$) containing 89.74 per cent of the theoretical amount of chromium is required to make the resistors for 1000 such furnaces, if 96.83 per cent of the chromium is recovered in the smelting process? *Ans.* 2510.666 kilos chromite.

125. When manganese dioxide is strongly heated it yields oxygen and Mn_3O_4. A certain amount of manganese dioxide on heating gave 1548.43 c.c. of oxygen, measured over water at 19.5° C. and 755.4 mm. pressure. How much manganese dioxide was heated and how much Mn_3O_4 was formed? *Ans.* 8.01 g., 7.027 g.

126. What weight of a 5 per cent solution (by weight) perchloric acid contains the same amount of oxygen as the manganese dioxide in **125**? *Ans.* 92.6 g.

127. A precipitate of ammonium chloroplatinate on ignition yielded 0.4633 g. of platinum. How many grams of ammonium chloride would yield this much platinum, if the ammonium chloroplatinate had been formed by mixing NH_4Cl and H_2PtCl_6? *Ans.* 0.2544 g.

128. How many grams of neodymium fluoride can be made by treating 15 g. of neodymium oxide Nd_2O_3 with hydrofluoric acid? *Ans.* 17.95 g.

129. Cuprous sulphide and silver nitrate react thus: $Cu_2S + 4AgNO_3 \rightarrow Ag_2S + 2Ag + 2Cu(NO_3)_2$, while cupric sulphide gives, with silver nitrate, silver sulphide and cupric nitrate alone. Moreover, silver and ferric nitrate react thus: $Ag + Fe(NO_3) \rightleftarrows AgNO_3 + Fe(NO_3)_2$. On these reactions a method is based for the determination of cuprous and cupric sulphides in a mixture. If 0.6414 g. of a mixture of these two sulphides yield 0.4319 g. of free silver (extracted as above by ferric nitrate) and the residue of silver sulphide contains 1.1462 g. of silver, calculate the percentage composition of the mixture. *Ans.* Cu_2S 0.3388 g., CuS 0.3026 g.

CHAPTER V.

GAS AND VAPOR DENSITIES: MOLAR WEIGHTS: ATOMIC WEIGHTS: SOLUBILITIES: SOLUTION CONCENTRATIONS: OSMOTIC PRESSURE: BOILING- AND FREEZING-POINT METHODS: VOLUMES OF GASES IN CHEMICAL REACTIONS.

Gas and Vapor Densities. The density of a gas or vapor is the weight of 1 c.c. at 0° and 760 mm. [111, *73*]. The measurement may be made at other temperatures and pressures, but the volume must be reduced by rule (p. 7) to 0° and 760 mm. Two methods of measurement are in use. In one a flask or vessel of known volume is used, and the weight of a gas or vapor which fills it is ascertained. In the other method, used chiefly for vapors, a known weight of the substance is taken, and the volume which its vapor occupies under known conditions of temperature and pressure are measured.

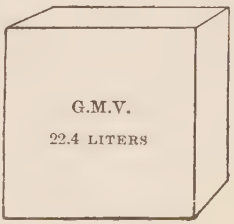

Fig. 1

The above is the physical method of expressing densities of substances. In chemistry, we calculate the weight of 22.4 liters (Gram-molecular volume, G.M.V.) at 0° and 760 mm., this weight being known as the **molecular weight** or the **molar weight,** or **one mole** of the substance. A cube, about 11.1 inches high (Fig. 1), represents this volume [236, *100*]. This volume holds 28.955 g. of air at 0° and 760 mm.

Example 15. A vessel of volume 205 c.c. holds 3.16 g. of a gas at 15° and 740 mm. What is the density and what the molecular weight?

$$205 \times \frac{273}{288} \times \frac{740}{760} = 194.3 \text{ c.c.}$$

1 c.c. (0° and 760 mm.) weighs $\frac{3.16}{194.3} = 0.01626$ g. = density.

194.3 : 3.16 : : 22,400 : x (= 365.9 g. = molar weight).

Example 16. Volume of vessel 205 c.c. Weight of vapor 2.1 g. at 110° and 752 mm.

$$205 \times \frac{273}{383} \times \frac{752}{760} = 146.1 \text{ c.c.}$$

1 c.c. weighs $\frac{2.1}{146.1} = 0.0143$ g. = density.

146.1 : 2.1 : : 22,400 : x (= 322 g. = molar weight).

The volume of the vessel at room temperature is smaller than that at the higher temperature of the measurement. In very exact work it is necessary, therefore, to correct the volume of the vessel to that at the higher temperature used, employing the coefficient of expansion of glass. In ordinary measurements, however, the measurement is made to ascertain whether the molecular weight is that corresponding to the simplest formula, or is some whole multiple of this value. This rather small correction is therefore not usually employed.

Example 17. 0.62 g. of the substance give 58 c.c. at 16° and 765 mm.

$$58 \times \frac{273}{289} \times \frac{765}{760} = 54.8 \text{ c.c.}$$

1 c.c. weighs $\frac{0.62}{54.8} = 0.0113$ g. = density.

54.8 : 0.62 : : 22,400 : x (= 253.4 g. = molar weight).

Example 18. The G.M.V. contains 7.06×10^{23} (or 7060_{21}) molecules of a gas. Find the weight in grams of one atom of mercury. In mercury vapor, for example, there are 200.6 g. of mercury in the G.M.V. One atom of mercury, therefore, weighs $200.6/7060_{21}$ g. = $0.0_{21}2844$ g.

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130. The weight of 1 l. of gas at 0° and 760 mm. is 5.236 g. What is the density referred (*a*) to air (air = 1) and (*b*) to hydrogen, and (*c*) what is the molecular weight? *Ans.* (*a*) 4.05; (*b*) 58.1; (*c*) 117.286.

131. The density of a gas, referred to air, is 6.7. What is the weight of 1 l., and what is the molecular weight? *Ans.* 8.66; 194.

The molecular weight of a substance is 65. What is the density referred to air, and what is the weight of 1 l.? *Ans.* 2.24; 2.9.

132. Find the weight in grams of one atom of tin, *e.g.*, in $SnCl_4$, which is volatile. *Ans.* $0.0_{21}158$ or 15.8×10^{-23}.

133. In an actual experiment 0.4618 g. of acetone vapor occupied a volume of 265.36 c.c. at a temperature of 75° C. and 640.3 mm. pressure (Porter, Jour. Am. Chem. Soc., **34,** 1290). What is its molecular weight? *Ans.* 59.05.

134. Calculate the weight of the gram-molar volume of oxygen (22.4 liters) from the following data: A test tube containing a mixture of potassium chlorate and manganese dioxide was heated in such a way that the oxygen driven off displaced 377.4 c.c. of water. The temperature of this water was 21° C. and the barometric pressure 747.4 mm. The test tube lost 0.4798 g. *Ans.* 31.98.

135. A glass balloon holding 249.7 c.c. is filled with dry carbon dioxide at 20° C. and 754 mm. pressure. This gas is now forced over, by means of CO_2 free air, into a Liebig bulb containing caustic potash. The bulb gains 0.4444 g. in weight. What is the weight of the G.M.V. of carbon dioxide? *Ans.* 43.13.

Atomic Weights. When an element gives volatile compounds, the atomic weight of the element is the smallest weight of the element found in 22.4 liters (0° and 760 mm.) of the vapor of any *compound* of the element. Thus, 22.4 liters of HCl weigh 36.46 g. and contain 35.46 g. of chlorine; the same volume of phosphorus trichloride (reduced by rule to 0° and 760 mm.) contains 137.38 g., of which 106.38 g. (3 × 35.46) is chlorine; and the same volume of free chlorine weighs 70.92. The G.M.V. of no compound of chlorine contains less than 35.46 g. of the element, and the atomic weight of chlorine is therefore 35.46.

Example 19. Phosphine contains phosphorus 91.123 per cent and hydrogen 8.877 per cent. The G.M.V. (22.4 l. at 0° and 760 mm.) contains 34.064 g. What weight of phosphorus does the G.M.V. contain?

$$91.123 : 100 : : x : 34.064, \text{ where } x = 31.04.$$

The G.M.V. of no compound of phosphorus contains less than 31 g. of the element and the phosphorus content of the G.M.V. of some other compounds is a multiple of this value by an integral number. Hence 31.04 is the atomic weight.

Dulong and Petit's Law, an Alternative Means of Determining Atomic Weights. It was first pointed out (1818) by Dulong and Petit, of the École Polytechnique in Paris, that when the **atomic weights of the elements were multiplied by the specific heats of the simple substances in the solid condition, the products were approximately the same in all cases.** In other words, the specific heats are inversely proportional to the magnitudes of the atomic weights. The table, in which round numbers have been used for the atomic weights, shows that

the product lies usually between 6 and 7, averaging about 6.4:

Element.	Atomic Wt.	Sp. Ht.	Product.
Lithium	7	0.94	6.6
Sodium	23	0.29	6.7
Magnesium	24.3	0.245	6.0
Silicon	28.3	0.16	4.5
Phosphorus (Yellow)	31	0.19	5.9
Calcium	40	0.170	6.8
Iron	56	0.112	6.3
Zinc	65.4	0.093	6.1
Bromine (Solid)	80	0.084	6.7
Gold	197	0.032	6.3
Mercury (Solid)	200	0.0335	6.7
Uranium	238	0.0276	6.6

Another way of expressing this law will give it greater chemical significance. The specific heats are the amounts of heat required to raise one gram, that is one *physical* unit, of each element through one degree. When we multiply this by the atomic weight, we obtain the amount of heat required to raise one gram-atomic weight of the element, that is, one chemical unit, through one degree. The values of this product are approximately equal. Since there are equal numbers of atoms in one gram-atomic weight of each element, it follows that: **Equal amounts of heat raise equal numbers of atoms of all elements in the solid form through equal intervals of temperature.**

Example 20. It will be seen at once that although the law of Dulong and Petit is purely empirical, it may nevertheless be **used for fixing the atomic weight of an element of which no volatile compounds are known.** We can always measure the equivalent (p. 16) with considerable exactness, and, when this has been multiplied by the specific heat of the free substance, we can see at a glance

what integral factor will raise the product to the neighborhood of 6.4. For example, analysis shows us that in calcium chloride the proportion of chlorine to calcium, using the known atomic weight of chlorine as one term of the proportion, is 35.46 : 20. If calcium is univalent, 20 is its atomic weight. If it is bivalent, two units of chlorine are combined with 40 parts of calcium, and 40 is its atomic weight. If it is trivalent, three units of chlorine are united with 60 parts of calcium, etc. All we learn in reference to the atomic weight of calcium from this analysis is that its value is 20 or some integral multiple of 20. Nor can we fix the upper limit, for we are unable to obtain the weight of a known volume of calcium chloride vapor and so determine the molecular weight. But the specific heat of solid calcium being 0.170, we multiply this number by 20, and get the product 3.4. This is only half large enough, so we find that 40 is the value for the atomic weight of calcium. The product is then 6.8, which agrees fairly well with the average for other elements. We decide, therefore, that the symbol Ca shall represent forty parts by weight. The formula of calcium chloride is therefore $CaCl_2$, and calcium is bivalent.

It will be seen that this does not supply us with a method of ascertaining chemical unit weights independently of any chemical experiment. We cannot measure the specific heat and use the quotient from division of this number into 6.4, for we do not know in advance that the product for the element will have exactly this value. It may be below 6, or it may be as high as 7. In the case of calcium, for example, $6.4 \div 0.17 = 37.65$. Now 37.65 is 5 per cent below the real value of the chemical unit, and even the roughest measurement of a chemical combining weight need never be more than 1 per cent in error. Hence the

atomic weight must be founded upon the determination of the equivalent, which can be measured with accuracy. The rule discussed in this section can be used only to ascertain what multiple of the equivalent shall be accepted as the atomic weight after the equivalent itself has been measured with care. In other words, this is a method of adjusting the result of chemical experimentation, and cannot supersede it altogether.

PROBLEMS.

136. The chloride of a new element contains 38.11 per cent of chlorine and 61.89 per cent of the element. The vapor density of the compound referred to air is 12.85. What is the atomic weight of the element, so far as investigation of this one substance can give it? What is its valence? *Ans.* 230.35; 4.

137. 205 c.c. of the vapor of aluminium chloride at 500° and 500 mm. weighs 0.568 g. What is the atomic weight of aluminium (20.31 per cent of molar weight), so far as this observation goes? *Ans.* 54.2.

138. 13 g. of iron combines with 16.74 g. of chlorine to form a chloride. What, according to Dulong and Petit's law, is the atomic weight of iron? *Ans.* 55.07.

139. 136 c.c. of silicon tetrachloride vapor at 70° and 752 mm. weighs 0.813 g. What is the atomic weight of silicon (10.75 per cent of molar weight), so far as this observation goes? *Ans.* 28.2.

140. 18 g. of zinc combine with 19.53 g. of chlorine to form a chloride. What, according to Dulong and Petit's law, is the atomic weight? *Ans.* 65.36.

Solubilities. The solubility of a substance is the weight in grams dissolving in 100 g. of water (almost exactly 100 c.c.) at 18°, or at some other specified temperature [181–182, *124*].

Example 21. If the solubility of barium chloride is given as 37.24 at 18°, what will be the amount dissolved in 832 g. of water at 18°? $37.24 : 100 :: x : 832$, where $x =$ 309.84 g. of barium chloride.

No general rule for calculating the solubility at another temperature is known. If a table, giving the solubilities of a given substance for every degree, or every two degrees, is available, the values for intermediate temperatures can be obtained by interpolation with reasonable accuracy. Thus, if the solubilities of sodium nitrate are 100 at 35° and 105 at 40°, the solubility at 37° is close to 102 g. If a diagram of solubilities at various temperatures is available [191, *131*, Appendix VII], then the value for any temperature within the range of the table can be read off.

Concentrations in Terms of a Normal Solution as Unity. A normal solution is one containing one equivalent of the radical or ion concerned in one liter of the solution (*not* in one liter of the solvent). Thus, 36.48 g. of hydrogen chloride HCl in one liter of solution is normal in respect both to hydrogen and chlorine [182, *124*]. For sulphuric acid, H_2SO_4, one-half the formula-weight, or 49 g., is an equivalent of each radical. If Na_2HPO_4 were used, one formula-weight (142 g.) per liter would make a solution normal with respect to the hydrogen radical; one-half of this amount (71 g.) would make a solution normal with respect to sodium; and one-third (47.3 g.) a solution normal with respect to PO_4.

Semi-normal (0.5 *N*) and decinormal (0.1 *N*) are solutions one-half and one-tenth normal, respectively. Higher concentrations, such as twice normal (2 *N*), are sometimes used.

Molar Solutions. A molar solution contains one mole of the solute in one liter of solution. Thus NaCl (58.46 g.) and $BaCl_2$ (208.29 g.), each dissolved to give one liter of the solution, are molar solutions.

PROBLEMS.

141. If 8.6 g. of potassium carbonate saturate 39 g. of water at 18°, what is the solubility of the substance? *Ans.* 22.05.

142. If 920 g. of water at 18° are saturated by 460 g. of potassium-hydrogen sulphate, what is the solubility? *Ans.* 50.

143. The solubility at 18° in 100 c.c. water of sodium bicarbonate $NaHCO_3$ is 9.6 and of mercurous chloride (calomel) is 0.0002. (*a*) Express each of these in terms of a molar solution as unity. *Ans.* 1.14; 8.5×10^{-6}. (*b*) Express also the concentration of the first, in terms of a normal solution as unity, with respect to each of the three radicals it contains. *Ans.* 1.14, 1.14, 2.28.

144. If 10 g. of ferrous chloride $FeCl_2$ are dissolved in 850 c.c. of water, the solution is oxidized by chlorine and diluted to 1000 c.c., what is the normal concentration of the solution? *Ans.* 0.2365 *N*.

145. How many grams of stannous chloride ($SnCl_2,2H_2O$) are required to make 18 g. of stannic chloride? *Ans.* 15.59.

146. 1200 c.c. of a solution contains 14.73 g. of potassium permanganate. What is its normality (*a*) with respect to K^+ ion; (*b*) with respect to its oxidizing power? *Ans.* (*a*) 0.0776 *N*; (*b*) 0.388 *N*.

147. If 500 c.c. of the above solution in **146** are acidified with sulphuric acid, reduced by sulphur dioxide and diluted to 750 c.c., what is the normality of the solution with respect to manganese? *Ans.* 0.1034 *N*.

148. How many c.c. of a half-normal potassium dichromate solution contain the chemical equivalent of the chromium in 25 c.c. of tenth-normal chromic chloride? *Ans.* 1.66 c.c.

149. How many c.c. of tenth-normal iodine solution are equivalent to 100 c.c. of a solution containing 25 g. of sodium thiosulphate, $Na_2S_2O_3,5H_2O$, in a liter? *Ans.* 100.72 c.c.

150. How many c.c. of tenth-normal sodium arsenite contain enough arsenite-ion to reduce 25 c.c. of a solution containing 10 g. of iodine per liter? *Ans.* 19.67 c.c.

151. What is the molar concentration of a solution which contains 48.77 g. of hydrogen chloride in 986.41 c.c. of solution? *Ans.* 1.383.

152. How many grams of sodium hydroxide are required to make 2800 c.c. of 3 times molar solution? *Ans.* 332.53 g.

153. A solution contains 17.46 g. of potassium chloride in 186.43 c.c. 25 c.c. of this solution is mixed with 25 c.c. of a solution con-

taining 14.43 g. of sodium chloride in 210 c.c. What is the total concentration of chloride in the mixture? *Ans.* Molar conc. KCl = 1.258. Molar conc. NaCl = 1.744. 1.258 + 1.744 divided by 2 = 1.501.

154. Into 250 c.c. of a solution of potassium chloride, 0.1748 g. of solid potassium chloride is dropped. 25 c.c. of this solution gives a precipitate of silver chloride weighing 2.8741 g. when the chloride is precipitated by adding excess of silver nitrate, acidified with nitric acid. What is the molar concentration of the original solution? *Ans.* 0.702 molar.

155. How many moles of sulphuric acid in a liter of a solution, 50 c.c. of which gives 8 g. of barium sulphate? What is the normality of this solution? *Ans.* 0.687; 1.374 *N*.

156. How many c.c. of hydrogen chloride, containing 18.43 g. in 171.43 c.c., are equivalent to 24.79 c.c. of the sulphuric acid in **155**? *Ans.* 11.39 c.c.

157. 18.29 c.c. of the sodium hydroxide in **152** are diluted until the concentration of the solution is 2.5 *N*. What is the new volume of the solution? *Ans.* 21.93 c.c.

158. How many c.c. of *N*/10 silver nitrate can be made by dissolving 28.421 g. of silver nitrate in water? *Ans.* 1625 c.c.

159. A solution is made by dissolving a certain quantity of nitric acid in water. 21.96 c.c. of this acid are required to neutralize 24.98 c.c. of *N*/2 sodium hydroxide. To what volume must 250 c.c. of this acid be diluted to make *N*/10 nitric acid? *Ans.* 1420 c.c.

160. The barium in 250 c.c. of *N*/20 barium hydroxide is precipitated as barium carbonate. What is the weight of the precipitate? *Ans.* 2.468 g.

161. If the barium carbonate in **160** were dissolved in hydrochloric acid and the carbon dioxide completely expelled from the solution, what volume would the CO_2 occupy if dried and collected over mercury, the temperature being 17° C. and the pressure 757.41 mm. *Ans.* 334.9 c.c.

162. In a Kjeldahl determination, 1.1261 g. of a certain material are decomposed by sulphuric acid. The ammonia formed is later expelled by distillation with sodium hydroxide. This ammonia is caught in *N*/10 H_2SO_4. 50 c.c. of this acid were placed in the receiver. After the distillation is complete it is found that 21.27 c.c. of 0.9846 *N* sodium hydroxide are required to neutralize the acid.

What percentage of nitrogen was in the original material? *Ans.* 3.61 per cent.

163. Six students each make a half normal solution of sodium carbonate. Calculate the real concentration of a solution made by mixing the following amounts of these solutions:

$$Ans.\ \text{Conc.} = \frac{581.6}{582.6} = 0.9982 \times N/2$$

A.....	121	c.c. (concentration = 1.02 $N/2$	$\doteq$ 123.7 c.c. $N/2$)
B.....	190	c.c. (concentration = 0.9894 $N/2$	$\doteq$ 187.5 c.c. $N/2$)
C.....	83	c.c. (concentration = 1.001 $N/2$	$\doteq$ 83.1 c.c. $N/2$)
D.....	10.10	c.c. (concentration = 0.9766 $N/2$	$\doteq$ 9.9 c.c. $N/2$)
E.....	100	c.c. (concentration = 0.9991 $N/2$	$\doteq$ 99.9 c.c. $N/2$)
F.....	78.5	c.c. (concentration = 0.9876 $N/2$	$\doteq$ 77.5 c.c. $N/2$)
	582.60		581.6

164. In standardizing a solution of hydrochloric acid, it was found that 25.93 c.c. exactly neutralized a solution made by dissolving 1.3281 g. of sodium carbonate in water. What is the concentration of this solution? *Ans.* 35.24 g. HCl per 1 l.

165. Enough moist calcium chloride ($CaCl_2,6H_2O$) to make 1 liter of tenth-normal calcium chloride solution is weighed out. A gravimetric determination shows that the solution is in reality 0.9464 times tenth-normal. How much water is contained in 125.47 g. of the wet salt? *Ans.* 6.77 g.

166. How many grams of ferric chloride ($FeCl_3,6H_2O$), 98.55 per cent pure, will be required to make 1250 c.c. of 3 times normal solution? *Ans.* 342.8 g.

167. 191 c.c. of three normal nickel chloride are diluted to 497 c.c. What is the concentration of the new solution? *Ans.* 1.153 *N*. How much of this new solution will be required to make 1000 c.c. of tenth-normal nickel chloride? *Ans.* 86.73 c.c.

168. What is the concentration in moles, and in equivalents, of a solution made by dissolving 17.44 g. of ammonium oxalate $(NH_4)_2C_2O_4,H_2O$ in water and diluting to 524.4 c.c. *Ans.* 0.234 *M*, 0.468 *N*.

169. 46.47 c.c. of sodium thiosulphate were required to react with 25 c.c of tenth-normal iodine solution, which had a factor of 0.9864. What is the normality of the thiosulphate solution from the iodometric standpoint? What is its normality with respect to the sodium radical? *Ans.* 0.053 *N*; 0.106 *N*.

170. How many grams of crystalline sodium thiosulphate (look up formula) would be required to make 1585.4 c.c. of the above solution? *Ans.* 20.85 g.

171. 0.2655 g. of copper were dissolved in nitric acid, evaporated with sulphuric acid, cooled, diluted and evaporated a second time. After cooling and diluting to 75 c.c. 10 c.c. of 40 per cent potassium iodide was added and the free iodine titrated with sodium thiosulphate, 42.37 c.c. being required. What is the normality of this thiosulphate solution. (Coltman, J. Ind. Eng. Chem., **7** (1915), 765.) *Ans.* 0.0985 *N*.

172. 8.5 mgm. of silver arsenate Ag_3AsO_4 is dissolved in 1 l. of the saturated solution at 20° C. What is the molar concentration of the salt? *Ans.* 0.0000184 *N*. What is the ionic concentration of the Ag^+, assuming complete dissociation? *Ans.* 0.0000552 *N*.

173. 39 milligrams of $AgIO_3$ are contained in 1 l. of its saturated solution at 20° C. Compare the molar solubility with that of Ag_3AsO_4. *Ans.* 0.000138 moles per l.; 7.5 times more soluble.

174. If a weight-normal solution of an undissociated compound boils at 100.52° under 760 mm. pressure, what is the boiling point of a solution containing 6 g. of boric acid in 100 g. of solvent? *Ans.* 100.523°.

175. If 100 g. of saturated boric acid solution contain 4.90 g. of boric acid at 21.6° C., what is the molar concentration of the solution? (Calculate on a wt. normal basis.) *Ans.* 0.873 *M*.

Osmotic Pressure. A solution, when separated from the pure solvent by a membrane permeable only by the solvent, exhibits a pressure known as osmotic pressure. In an infinitely dilute solution, the osmotic pressure is the same as the gaseous pressure which the same amount of the solute, if present as a gas in the same volume, would exert. This law holds, approximately, for very dilute solutions, but not for solutions such as are commonly used. In symbols, the law is $PV = RT$, where P is the osmotic pressure, V the volume containing one gram molecule, R is the same as the gas constant, namely 0.08204, when P is in atmospheres and V in liters, and T is the absolute temperature (327–333, St. 8–32).

That this law cannot be used for solutions commonly used, may first be shown. Thus, an 0.1 molar solution of sugar in water at 0° gives an osmotic pressure of 2.42 atmos. The value calculated from the above equation is $P = 0.08204 \times 273/10 = 2.24$ atmos. For a molar solution of sugar, the observed value at 0° is 24.45 atmos., and the calculated value 22.4 atmos. For a 2.2 molar solution, the observed value is 133.74 atmos., while the calculated value is only 49.33 atmos.

A better formula, for a non-ionized substance, such as sugar, is:

$$P_{os} = \frac{RT}{v} \log_e \frac{1}{x}.$$

Here, P_{os} is in atmospheres, $R = 0.08204$, T is the absolute temperature, v is the volume *in liters* of one molecular weight of the solvent, and x is the molar fraction of the solvent in the whole solution.

With water, and other partly associated liquids, as solvents, the answer is not exactly equal to the measured value. This is partly because we do not know how much $(H_2O)_2$ and $(H_2O)_3$ are contained in the water. If there is any change of volume or of temperature when the solute is dissolved, these factors also cause discrepancies.

Example 22. Calculate the osmotic pressure of 0.5 *M* sugar solution at 0°. The molar weight of sugar is 342 g., so this solution contains 171 g. The sp. gr. of sugar is 1.588, so 171 g. occupy 107.7 c.c. As there is little change of volume when sugar dissolves, one liter of the solution contains 1000 c.c. − 107.7 c.c. = 892.3 c.c. water = 49.5 moles of water. In solution, one mole of sugar forms a hydrate $C_{12}H_{22}O_{11},6H_2O$. One-half mole will therefore remove $3H_2O$ from the solvent. Hence x, the molar frac-

tion of the solvent = 49.5 − 3/49.5 − 3 + 0.5 = 46.5/47. Thus:

$$P_{os} = \frac{0.08204 \times 273^\circ}{18/1000} \log_e \frac{47.0}{46.5}$$

Log 0.08204	$= \bar{2}.91403$	$\text{Log}_{10}\,47.0$	$= 1.67210$
Log 273	$= 2.43616$	$\text{Log}_{10}\,46.5$	$= 1.66745$
Log 1000	$= 3.00000$		0.00465
Log 0.00465	$= \bar{3}.66745$		
Log 2.303	$= 0.36229$ (to convert to base e)		
	2.37993		
Log 18	1.25527		
	1.12466		

P_{os} = 13.325 atmos. (obsd. value 11.90).

PROBLEMS.

176. If the osmotic pressure of a 0.1 weight-normal solution of cane sugar is 2.452 atmospheres at 5° C. and 2.634 atmospheres at 25° C., how does osmotic pressure change with the absolute temperature? Use above results to prove your answer. *Ans.* Increases 138 mm. for rise of 20°. Ratio of Abs. temps. 1.072; of pressures 1.074.

177. If the osmotic pressure of an 0.2 weight-normal solution of cane sugar at 10° C. is 4.893 atmospheres, what is the osmotic pressure of an 0.3 weight-normal solution of the same substance at 10° C.? *Ans.* Approximately 7.34 atmos.

178 (*a*). What is the molar fraction of water in a cane sugar solution which gives an osmotic pressure of 6 atmos. at 5° C.? *Ans.* 0.9953.

(*b*) How many grams of sugar are dissolved in 100 c.c. of the solution mentioned in 178 (*a*)? *Ans.* 8.265 g.

Elevation in the Boiling-Point of a Solvent by a Solute. The boiling-point of a solution, containing a non-volatile solute, is elevated above that of the pure solvent. The elevation, for one mole of a non-ionized solute in

1000 grams of solute is as follows: Water +0.52°, benzene 2.66°, phenol (carbolic acid) 3.04°.

The relations to concentration are as follows:
Observed elevation in solution

$$= \text{Molar elevation} \times \frac{\text{wt. of solute}}{\text{mol. wt. of solute}} \times \frac{1000}{\text{wt. of solvent}}.$$

Example 23. What elevation in the boiling-point will be given by 50 g. of sugar (molar wt. 342) in 1 liter of water?

$$\text{Obsd. Elevn.} = 0.52 \times \frac{50}{342} \times \frac{1000}{1000} = 0.076°.$$

Depression in the Freezing-Point of a Solvent by a Solute. The freezing-point of a solution, containing a solute which does not enter into the crystals of the solvent when the latter begins to freeze, is depressed below that of the pure solvent. The depression, for one mole of a non-ionized solute in 1000 g. of the solvent, is as follows: Water 1.86°, benzene 5°, phenol (carbolic acid) 7.3°. The relations to concentration are the same as those for boiling-points (above). Simply substitute depression of f.-p. for elevation of b.-p.

For example, what depression in the f.-p. will be given by 13 g. of methyl acetate (molar wt. 88) dissolved in 500 g. water?

$$\text{Obsd. depression} = 1.86° \times \frac{13}{88} \times \frac{1000}{500} = 0.55°.$$

Example 24. If a substance of molar weight 102 is dissolved in benzene, and gives a boiling-point elevation of 0.1°, what weight of the substance is dissolved in 1000 g. of benzene?

$$0.1° = 2.66 \times \frac{x}{102} \times \frac{1000}{1000}. \quad x = 3.83 \text{ g.}$$

Example 25. If 1 g. of a substance dissolved in 30 g. of phenol give a b.-p. elevation of 0.21°, what is the molar weight of the substance?

$$0.21° = 3.04° \times \frac{1}{x} \times \frac{1000}{30}. \quad x = 482.$$

Example 26. If a substance of molar weight 201 is dissolved in benzene, and gives a depression in the freezing-point of 0.2°, what is the weight of the substance dissolved in 1000 g. of benzene?

$$0.2 = 5° \times \frac{x}{201} \times \frac{1000}{1000}. \quad x = 8.04 \text{ g.}$$

Example 27. If a solution of 3 g. of a substance, dissolved in 50 g. phenol, depresses the freezing-point 0.7°, what is the molar weight of the substance?

$$0.7 = 7.3 \times \frac{3}{x} \times \frac{1000}{50}. \quad x = 626.$$

PROBLEMS.

179. What depression in the f.-p. of water will be produced by dissolving 10 g. of bromine in 1 kg. of this solvent? *Ans.* 0.116°.

180. What depressions in the f.-p. of benzene and of phenol would be produced by 10 g. of bromine to 1 kg. of the solvent, if no chemical action took place? *Ans.* 0.31°; 0.456°.

181. What is the molecular depression-constant of a solvent in which 5 g. of iodine in 500 g. of the solvent lowers the f.-p. 0.7°? *Ans.* 17.8°.

182. If 5 g. of a substance, dissolved in 1000 c.c. of water, give a solution freezing at −2°, what is the molecular weight of the substance? *Ans.* 4.65.

183. 6 g. of a substance when dissolved in 200 c.c. of water give a boiling-point of 102.6°. What is the molecular weight of the substance? *Ans.* 6.

184. 1.6 g. of naphthalene $C_{10}H_8$ when dissolved in 25 g. of benzene (freezing-point 5.48°) give a solution which freezes at 3.03°. When 2.44 g. of another substance are dissolved in the same amount of benzene, the solution freezes at 3.52°. What is the molecular weight of the latter substance? *Ans.* 244.

185. If the boiling-point of acetone is raised 1.09° by 0.6749 g. camphor in 6.81 g. acetone, what is the molecular weight of camphor? (Boiling-point constant of acetone is 1.67°.) *Ans.* 151.8.

186. What weight of glucose, $C_6H_{12}O_6$, must be dissolved in a liter of water to give a lowering of the freezing point of 0.1° C.? *Ans.* 9.81 g.

Molecular Equations. The following shows **the interpretations to which the molecular equation is subject:**

	H_2	+	Cl_2	→	$2HCl$.
Weights:	2.016 g.		70.92 g.		2×36.468 (= 72.936) g.
Volumes:	22.4 l.		22.4 l.		2×22.4 l.
Molecules:	1		1		2

The weights, although doubled, show the same proportions, so that questions of weight are answered as easily as before. These weights, however, being molecular weights, or multiples thereof, can be translated at once into *volumes*, and **questions about volumes can also be answered.** Finally **the relative numbers of each kind of molecules can be read from this equation,** for the coefficients in front of the formulæ represent these numbers. Where no coefficient is written, 1 is to be understood. The application of these properties of molecular equations is illustrated below. Before applying these equations, however, we must first learn how to make them.

The Making of Molecular Equations. To make a molecular equation, we first make an ordinary equation. An equation like that for the interaction of oxygen with

hydrogen chloride (Deacon's process): $2HCl + O \rightarrow H_2O + 2Cl$, is the result. Then we adjust the equation so that molecular formulæ are used throughout. 2Cl becomes at once Cl_2. The oxygen, however, must also appear as O_2, or a multiple of this, in such equations. Hence the whole equation must be multiplied by 2:

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2.$$

Again, the equation for the preparation of chlorine from potassium permanganate and hydrochloric acid becomes:

$$2KMnO_4 + 16HCl \rightarrow 8H_2O + 2KCl + 2MnCl_2 + 5Cl_2.$$

Every equation containing an *odd* number of atoms of a substance whose molecules are *diatomic* must be multiplied by 2. Again, mercuric oxide decomposes to give mercury vapor and oxygen, and the molecules of mercury are monatomic and those of oxygen diatomic, so we write:

$$2HgO \rightarrow 2Hg + O_2.$$

Finally, the formulæ of substances which are solid or liquid, and cannot be easily vaporized, are written in the simplest terms. Thus, since substances like the copper in the following equation are involatile, the molecular weights of such substances are unknown, and their molecular formulæ likewise: $2Cu + O_2 \rightarrow 2CuO$. Furthermore, in the case of substances which can be volatilized, although the molecular weights and molecular formulæ may therefore be known, we do not usually employ the molecular formulæ if the substance is not used in the form of vapor in the laboratory. Thus, the molecular formula of phosphoric anhydride is P_4O_{10}. But we generally make, and use, only the solid form, and not the vapor, in actual work. Hence the action with water is

usually written with P_2O_5, rather than in the form: $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$.

The applications of the properties of **molecular equations (which will be used exclusively hereafter)** may now be illustrated in detail.

Applications: To Arithmetical Problems. When a problem in regard to **weights** of material used or produced in a given action is to be solved, the molecular equation is to be written and the weights inserted beneath the formulæ. The mode of calculation has been described already (p. 14).

When a problem involving **weights and volumes** is to be solved, the molecular equation is to be written, and both the weights and volumes are to be inserted. Note, however, that the volumes of the substances which are *in the gaseous condition* only are inserted.

Example 26. What volume of oxygen is obtained from 60 g. of potassium chlorate? The molecular equation, made as shown above, together with the full interpretation, are as follows:

	$2KClO_3$	$\rightarrow$	$2KCl$	$+$	$3O_2$.
Weights:	$\underbrace{2\,(39.1 + 35.46 + 48)}$		$\underbrace{2\,(39.1 + 35.46)}$		$\underbrace{3 \times 32}$
	245.12 g.		149.12 g.		96 g.
Volumes:					3×22.4 l.
Given:	60 g.				x l.

Observe that no volumes are given under the chlorate and chloride of potassium. This is because their volumes in the *gaseous* condition can be of no practical use, since they are solids which are melted, *but not vaporized* during this, or any action in which we employ them. Note also that the data *given* in the problem are inserted, and x l. is placed under the oxygen. Now, as to the problem in

hand, it is concerned with a weight of potassium chlorate and a volume of oxygen. Reading from the equation, our information on *these* points is that 245.12 g. of potassium chlorate give 67.2 liters (observe that the *coefficients* are used, as well as the molecular weights, in these numbers) of oxygen at 0° and 760 mm., and the question is, What volume will 60 g. give? By proportion, 245.12 : 67.2 : : 60 : x, where $x = 16.4$ liters. If a different temperature and pressure had been specified, either the volume in the equation, or the answer, would have had to be converted by rule to the given conditions.

It saves time not to write out, as above, the whole interpretation, but only the parts required. For example, if the question is: What volume of chlorine is needed to give 25 g. of aluminium chloride, we may, if we choose, omit all the data excepting the volume of the chlorine and the weight of the aluminium chloride, thus:

$$\begin{array}{ccccc} 2Al & + & 3Cl_2 & \rightarrow & 2AlCl_3 \\ & & 3 \times 22.4\,l. & & 2 \times 133.48\,g. \\ & & x\,l. & & 25\,g. \end{array}$$

The volume of chlorine required is $3 \times 22.4 \times 25 \div (2 \times 133.48)$ liters. These illustrations show the method of calculating actual volumes.

If the question concerns **relative volumes** only, then it is simplest to use the interpretation of the equation in terms of molecules. For example, What relative volumes of hydrogen chloride and oxygen are required in Deacon's process? The molecular equation is (p. 41):

$$4HCl + O_2 \rightarrow 2H_2O + 2Cl_2.$$

MOLECULES: 4 1 2 2

Since equal numbers of molecules of gases occupy equal volumes, the proportion 4 molecules of hydrogen chloride

to 1 molecule of oxygen shows the ratio to be 4 : 1 by volume. Similarly, every 4 molecules of hydrogen chloride give 2 molecules of chlorine, so that the ratio of these substances by volume is 4 : 2, or 2 : 1.

In regard to the water, since that is not a gas at common temperatures, the question, if asked, must be more specific: What are the relative volumes of *steam* and chlorine in the product, as commonly delivered by the action at 400°? It is 2 : 2, or 1 : 1. What are the relative volumes of water and chlorine, after the products have cooled to room temperature? The water is no longer a gas, so that it occupies, relatively, almost no volume.*

What is the total volume-change in the foregoing action above 100°? It is a change from 5 molecules to 4. The volume changes in the same ratio. But at 0° the volume-change is from 5 volumes to 2, for the water does not appreciably add to the volume of the products.

When we know the molecular formulæ of the single substances concerned **in an action,** the equation can be made, and **the relative volumes determined, without actual measurement.** For example: What volume-change will be observed when a mixture of carbon monoxide and oxygen has exploded, and the temperature has once more reached that of the room? The molecular formulæ are CO, O_2, and CO_2. The equation representing the *weights* is $CO + O \rightarrow CO_2$. The molecule of oxygen,

* Of course if an exact answer *must* be given, it can be given. But for this we require the weight and specific gravity of the product. Thus, $2H_2O$ represents 2×18 g. of water. The sp. gr. of water is 1. Therefore the volume of water formed is 36 c.c. The volume of $2Cl_2$ is 2×22.4, or 44.8 liters at 0°. The ratio of water to chlorine by volume at 0° is therefore 36 : 44,800. But, as a rule, we simply give the volumes of solids and liquids as *zero,* compared with those of the gases concerned in the same action.

however, being O_2, we cannot employ less than this quantity in a molecular equation, so that the equation becomes:

$$2CO + O_2 \rightarrow 2CO_2.$$

Three molecules, therefore, give two, throughout the whole mass, and therefore three volumes will become two, if the pressure and temperature are the same at the beginning and end of the action.

If we remember that all volatile compounds of carbon and hydrogen burn to form water and carbon dioxide, the molecular equation for any such combustion may easily be made, and the volumes of all the materials ascertained. When water is a product, only its volume as steam is given by the equation.

Knowing by heart the molecular formulæ of gaseous substances, as we must know them for many purposes, it is unnecessary to burden our minds with other data in regard to **the relative densities of gases.** Is hydrogen chloride HCl heavier or lighter than carbon dioxide CO_2? These formulæ represent the weights of equal volumes (22.4 l.), namely 36.46 g. and 44 g., respectively. Hence the former gas is a little lighter. Remembering that the G.M.V. of **air** weighs 28.955 g., we can compare the weight of any gas with that of air in the same way.

Example 27. What are the relative weights of acetylene (C_2H_2) and sulphur dioxide SO_2 as compared with air? The G.M.V. cube holds formula-weights of the first two, namely 26 g. and 64 g., and 28.955 g. of air. Hence acetylene is a little lighter than air, and sulphur dioxide more than twice as heavy.

Applications: To Cases of Dissociation. Several gases or vapors yield smaller values for their densities, and therefore molecular weights, when the densities are meas-

ured at higher temperatures. This indicates that the molecules have become lighter, and can only mean that decomposition has taken place in consequence of the heating. Behavior of this kind is shown both by compounds and by simple substances.

For example, **phosphorus pentachloride** PCl_5, although a solid, can be converted into vapor without much difficulty. Its molecular weight, if it underwent no chemical change during the volatilization, would be $31 + 177.3 = 208.3$. The density actually observed at 300° and 760 mm. pressure gives by calculation not much more than half this value. The direct inference from this is, that the molecules have only half the (average) weight that we expected: or, in other words, are twice as numerous as we expected. The explanation is found when we examine the nature of the vapor more closely. We find that it is a mixture of phosphorus trichloride and free chlorine, resulting from a chemical change according to the equation: $PCl_5 \rightleftarrows PCl_3 + Cl_2$. The low value of the density thus tells us that dissociation has taken place. From the value of the density at various temperatures, we may even calculate the proportion of the whole material which is dissociated. At 300° it is 97 per cent; at 250°, 80 per cent; and at 200°, 48.5 per cent. Thus, when the temperature is lowered, progressive recombination takes place and the proportion dissociated becomes less. Finally the vapor condenses and yields the original solid.

PROBLEMS.

187. If a new form of oxygen were found, such that one volume of it required four volumes of hydrogen to produce water, what would be its molecular formula? What would be the weight of 22.4 l.? *Ans.* O_4, 64 g.

188. What volume of oxygen at 10° and 750 mm. is obtainable by heating 50 g. of barium peroxide? *Ans.* 3.4701 l.

189. What volume of oxygen at 20° and 760 mm. is required to convert 16 g. of iron into dehydrated rust Fe_2O_3? *Ans.* 5166.3 c.c.

190. Write out the molecular equations for the interactions of methane and chlorine giving CH_3Cl; and for the burning of phosphorus (vapor) in oxygen. Deduce the volume relations of the initial substances, and of the products, at 0° and 100° in each case. *Ans.* 1 : 1 = 1 : 1 (0° and 100°); 1 : 5 = solid (0° and 100°).

191. Write out the molecular equations for the interactions of acetylene and oxygen, and of alcohol vapor (b.-p. 78°) and oxygen. Deduce the volume relations of the initial substances and of the products at 0° and at 100° in each case. *Ans.* 2 : 5 = 4 : 0 (0°) = 4 : 2 (100°); 0 : 3 = 2 : 0 (0°), 1 : 3 = 2 : 3 (100°).

192. The molecular weight of cyanogen is 52.08. What is its density referred to air, and what the weight of 1 l. at 0° and 760 mm.? It contains 46.08 per cent carbon and 53.92 per cent nitrogen. What is the formula of the substance? Exploded with oxygen it forms carbon dioxide and free nitrogen. What will be the relative volumes of the materials before and after the interaction? *Ans.* 1.8 (air = 1) 2.32 g.; C_2N_2; 1 : 2 = 2 : 1.

193. What are the relative weights of equal volumes of hydrogen sulphide H_2S, and hydrogen iodide HI, compared with air? *Ans.* 34.076 : 127.9 : 28.955.

194. At 1700° the average molecular weight of phosphorus is 91 (p. 47). What percentage of molecules of P_4 has been dissociated into P_2? *Ans.* 36.26 per cent.

195. If it were possible to remove all the water from 500 c.c. of a normal solution of hydrogen chloride at 20° C., so that the gas left would occupy the same volume as did the solution, what would be its pressure? *Ans.* 24.04 atmos.

196. A spark discharge is allowed to pass through a flask which holds 500 c.c. of dry ammonia at 20° and 748 mm. The spark is continued until 50 per cent of the ammonia is decomposed. What is the pressure within the flask at 20° C.? *Ans.* 1122 mm.

197. Using the tables of "atomic" and equivalent weights on p. 16, write an equation expressing the following facts: 18.44 g. of one of the chlorides of copper is dissolved in more than sufficient water to effect its solution. A few drops of hydrogen chloride solu-

tion, containing in all 0.46 g. HCl, is added, and the solution saturated with hydrogen sulphide. The excess of hydrogen sulphide is expelled. The precipitate in the vessel is carefully filtered off, and washed with a solution of hydrogen sulphide, the filtrate and all the washings being saved. The precipitate is ignited in a stream of hydrogen, in a Rose crucible, after having been treated with a little sulphur. After repeated ignition in this manner, its weight is found to be 13.10 g. The filtrate and wash water is now freed of hydrogen sulphide by boiling, and a solution of sodium hydroxide, of such concentration that 1000 c.c. contains 200 g. of the base, added to neutrality, 57.63 c.c. being required. This solution is then made slightly acid with nitric acid, a very slight excess of silver nitrate is added and the precipitate filtered off, washed, dried and weighed. Its weight is 41.18 g. Write the equation to show (*a*) the molar fractions of all substances entering into the reaction and (*b*) to show the equation in its *simplest* form. *Ans.* (*a*) $CuCl_2$ 0.137, CuS 0.137, NaOH 0.288, $AgNO_3$ 0.287; (*b*) $CuCl_2 + H_2S \rightarrow CuS + 2HCl$.

198. What volume of hydrogen sulphide, measured at 739 mm. and 24° C., will contain the same weight of sulphur as that contained in the 13.10 g. of material mentioned in **197** above? *Ans.* 3433.54 c.c.

199. What weight of zinc chloride (anhydrous) contains the same weight of chlorine as the 18.44 g. of the copper compound in **197**? *Ans.* 18.671 g.

CHAPTER VI.

CHEMICAL EQUILIBRIUM.

Formulation of Chemical Equilibrium. When chemical equilibrium has been reached, the speeds of the forward and reverse actions have become equal. Thus, when the vapor of phosphorus pentachloride is kept at a fixed temperature and pressure, this state is quickly reached. The equation and equilibrium constant are:

$$PCl_5 \rightleftarrows PCl_3 + Cl_2 \text{ and } K = \frac{[PCl_3]_{eqm.} \times [Cl_2]_{eqm.}}{[PCl_5]_{eqm.}}.$$

If one gram-molecule of pure PCl_5 is taken, and x is the fraction dissociated, and v the volume occupied by the whole, the $[PCl_3]_{eqm.} = [Cl_2]_{eqm.} = \frac{x}{v}$, and $[PCl_5]_{eqm.} = \frac{1-x}{v}$.

Thus $K = \frac{x^2}{(1-x)v}$.

Measurement of the vapor density enables us to calculate the proportion dissociated. Thus at 300° the density is 107.29, at 250° it is 125.0, at 200° it is 157.82. The density undissociated (0° and 760 mm.) is $31.03 + 5 \times 35.46 = 208.34$, that for complete dissociation into $PCl_3 + Cl_2$ is half as much, or 104.17. The values given lie between these extremes.

Example 28. Find the fraction dissociated at 300°. $y = \frac{k}{1+x}$. Where the fraction dissociated (x) is zero, y, the molecular weight, is 208.34. Hence $k = 208.34$. When

$y = 107.29$ at 300°, we have: $107.29 = \frac{208.34}{1+x}$. $x = 0.9418$ or 94.18 per cent as the fraction dissociated.

At 250°, $y = 125.0$. $125 = \frac{208.34}{1+x}$. $x = 66.67$ per cent.

At 200°, $y = 157.82$. $157.82 = \frac{208.34}{1+x}$. $x = 32.01$ per cent.

Example 29. Alternative method. Since x dissociated moles of PCl_5 give $2x$ new moles, and $1 - x$ moles are left undissociated, the total number of moles is $1 - x + 2x = 1 + x$ moles. Now the concentrations are inversely proportional to the densities. Hence at 300°: $1 : 1 + x :: 107.29 : 208.34$, where $x = 0.9418$ or 94.18 per cent.

Substituting the values at 250° in the formula, we have $x = 0.6667$ and $1 - x = 0.3333$. Hence,

$$K = \frac{0.6667^2}{0.3333\,v}. \quad \text{Here } v = \frac{1.6667 \times 22.4 \times 523}{273}.$$

Hence $$K = \frac{0.6667^2}{0.3333 \times 71.52} = \frac{1}{53.6}.$$

This result means that, the union of PCl_3 and Cl_2 would proceed 53.6 times as fast as the dissociation, if each of the three substances were present in unit concentration (which, at equilibrium, as the data show, they are not), and each action could proceed independently, without reversal [297–303, *184*, St. 90–97].

PROBLEMS.

200. Calculate the values of K for phosphorus pentachloride at 300° and at 200°, and state what the result in each case means. *Ans.* 1/6, 1/3401.

201. At 345° the vapor of sulphuric acid is dissociated to the extent of 0.51. Find the value of the dissociation constant, and interpret it. *Ans.* 1/144.

202. At 1100° the fraction of iodine vapor (I_2) dissociated into atomic iodine (I) is 0.31. Find the dissociation constant and interpret it. *Ans.* 1/98.2.

Cases in which no Change in Volume Occurs. When hydrogen iodide dissociates: $2HI \rightarrow H_2 + I_2$, the number of molecules is unchanged, and the volume is unaltered. In this case:

$$\frac{[H_2]_{eqm.} \times [I_2]_{eqm.}}{[HI]^2_{eqm.}} = K.$$

Example 30. Thus, at 445°, the fraction dissociated is 0.21. Hence in every 100 molecules 10.5 are H_2, 10.5 are I_2 and 79 are HI. Thus $K = 0.105^2 \div 0.79^2 = \frac{1}{56.6}$.

PROBLEMS.

203. Calculate the value of K for HI at 508°, at which 24 molecules per hundred are dissociated, and 76 are undissociated, and interpret the result. *Ans.* 1/40.

204. Calculate the equilibrium constant for Deacon's reaction: $4HCl + O_2 \rightleftarrows 2H_2O + 2Cl_2$, in which, at 370°, 0.8 parts of the HCl are changed, and 0.2 parts are unchanged. *Ans.* $K = 0.6488$.

Presence of an Excess of one Interacting Substance. Suppose that we have hydriodic acid at 445°, and that, without increasing the volume, we introduce an amount of iodine equal to that liberated in the action.

Example 31. This means that, before action can occur, there are 79 mols HI, 10.5 mols H_2, and 21 mols I_2, and $0.105 \times 0.21 \div 0.79^2 = \frac{1}{28.6}$. To restore the equilib-

rium constant to its proper value, some of the $H_2 + I_2$ must interact to form HI, thus diminishing the numerator and increasing the denominator, until the value becomes $\frac{1}{56.6}$, as before. Note that equal numbers of molecules of H_2 and I_2 are removed (say x) and that $2x$ mols of HI are produced therefrom:

$$\frac{(0.105 - x) \times (0.21 - x)}{(0.79 + 2x)^2} = \frac{1}{56.6} = \frac{x^2 - 0.315x + 0.02205}{4x^2 + 3.16x + 0.6241}.$$

$$4x^2 + 3.16x + 0.6241 = 56.6x^2 - 56.6 \times 0.315x + 56.1 \times 0.02205 = 56.6x^2 - 17.829x + 1.248.$$

$$52.6x^2 = 20.989x + 0.624 = 0.$$

Solving for x, we find

$$x = \frac{20.989 \pm \sqrt{(20.989^2 - 4 \times 52.6 \times 0.624)}}{2 \times 52.6}$$

$$= 20.989 \pm 17.59 = 38.58 \text{ mols or } 3.4 \text{ mols.}$$

Thus $$\frac{(0.105 - 0.386) \times (0.21 - 0.386)}{(0.79 + 0.7716)^2}$$

or $$\frac{(0.105 - 0.034) \times (0.21 - 0.034)}{(0.79 + 0.068)^2} = \frac{1}{56.6}.$$

Calculation shows that the second result (3.4 mols) is correct, giving $\frac{1}{58.9}$. Thus at equilibrium there are 0.071 parts H_2, 0.176 parts I_2, and 0.858 parts HI in a total of 1.105 parts.

PROBLEMS.

205. The reaction (Lewis and Edgar, J. Am. Chem. Soc., **33** (1911), 292), $H^+ + NO_3^- + H_2O + 2NO \rightleftarrows H_2O + 3HNO_2$, is one in which the activity of the water and of the nitric oxide may be regarded as constant at 25° C. and at 760 mm. If the nitric oxide

is saturated with water vapor at 25° and the condition of equilibrium is reached, when concentrations are as below, calculate the equilibrium constant for this reaction: Conc. nitrous acid = 0.04942 M; of nitrate-ion 0.06983 M; of hydrogen-ion 0.07015. *Ans.* 0.0246.

206. Jones and Hartman (J. Am. Chem. Soc., **37** (1915), 241) find that the equilibrium constant for the reaction $1^- + 1_2 \rightleftarrows 1_3^-$ has an average value of 710×10^{-6} at 0° C. If the concentration of I^- is 0.04498 and of I_3^- is 0.04181, what is the concentration of molecular iodine? *Ans.* 0.00066.

207. In the reaction $CO + S \rightleftarrows COS$ (Lewis and Lacey, J. Am. Chem. Soc., **37** (1915), 1976), it is found that at 302° C., when equilibrium is reached, 0.8297 moles of carbon oxysulphide and 0.00413 moles of carbon monoxide are present. What is the equilibrium constant? *Ans.* 201.

208. If in the reaction $A + B \rightleftarrows C + D$, at 10° C., equilibrium is reached when concentration $A = 0.004$ moles per liter, $B = 0.015$ moles per liter, $C = 0.020$ moles per liter, $D = 0.003$ moles per liter, calculate the equilibrium constant. *Ans.* 1.00.

209. If in **208** above we start with concentrations of A and B each equal 1 mole per liter, find the concentration of each component when equilibrium is reached. *Ans.* 0.5 moles per liter.

210. At 3300° Abs., according to Langmuir (Jour. Am. Chem. Soc., **34** (1912), 860), equilibrium is reached in the equation $H_2 \rightleftarrows 2H$, when the concentration of the atomic hydrogen is 2.51×10^{-6}. Calculate the dissociation constant, if the concentration of molecular hydrogen is 1.19×10^{-6}. *Ans.* 5.27×10^{-6}.

211. From the above data in **210,** calculate the degree of dissociation. *Ans.* 68 per cent.

212. According to A. Smith and Lombard (Jour. Am. Chem. Soc., **37** (1915), 24), saturated ammonium chloride vapor, at 320° C., has a vapor density corresponding to 0.00759 moles per liter. If it were undissociated, the value should be 0.01239. Calculate the degree of dissociation. *Ans.* 63.1 per cent.

213. G. M. P. Smith (Jour. Am. Chem. Soc., **35** (1913), 39) has studied the reaction $KHg_m + NaCl \rightleftarrows KCl + NaHg_m + (m - n)\,Hg$ in dilute amalgam solutions. Formulate the equilibrium relations (mercury assumed constant in amount), and calculate C, the equilibrium constant, if at 18° C. the total concentration of salts is 0.2 N, the equivalent fractions of sodium and potassium chlorides

are each 50 per cent, and the molar fraction of compounds in the amalgam are: For KHg_m 0.3166; for $NaHg_m$ 0.6834. *Ans.* 0.463.

214. Koref (Zeit. Anorg. Chemie, **66,** 73–92) states that, in the reaction $C + S_2 \rightleftarrows CS_2$, the equilibrium constant at 823° is 0.078. Formulate the mass action equation and calculate the amount of sulphur in equilibrium with carbon disulphide at 823°, if the concentration of the latter is 0.85 moles per liter. *Ans.* 0.0663 moles per liter.

215. If at 1557° Abs. and 721 mm. pressure, bromine vapor is dissociated 18.3 per cent, according to the equation $Br_2 \rightleftarrows 2Br$, calculate the partial pressure of the Br_2 molecules. *Ans.* 498 mm.

216. Von Falckenstein (Zeit. physikal Chemie, **68,** 270) states that, at 1222° C., hydrogen bromide is dissociated to the extent of 1.08 per cent into H_2 and Br_2. Formulate the law of mass action for this dissociation, show why the concentration does not have to be taken into account, and calculate the dissociation constant. *Ans.* 1/8391.

CHAPTER VII.

FARADAY'S LAWS; ELECTROLYSIS; SPECIFIC CONDUCTIVITY; EQUIVALENT CONDUCTIVITY; DEGREES OF DISSOCIATION; DISSOCIATION CONSTANTS.

Faraday's Laws. Electrical energy is expressed as the product of two factors, voltage and quantity of electricity (coulombs). Faraday's laws state that the quantity of an electrolyte decomposed by a current is proportional to the quantity of electricity; and that equal quantities of electricity decompose chemically equivalent quantities of different electrolytes. Sufficient voltage to decompose each substance must be used. The quantity of electricity required to decompose one gram-equivalent of a compound (*e.g.* 36.46 g. of HCl or 134.5/2 g. of $CuCl_2$) is 96,504 coulombs (one Faraday) [350, *231*, St. 58].

A current of 1 coulomb per second is called 1 ampere.

No. of volts × No. of amperes = No. watts.

Example 32. A current passed for 10 minutes through dilute hydrochloric acid, already saturated with chlorine, liberated 40 c.c. of gas at 18° C. and 752 mm. What number of coulombs was used, and what was the average amperage of the current?

At 0° and 760 mm., the volume occupied by the gas is

$$40 \times \frac{752}{760} \times \frac{273}{291} = 37.1 \text{ c.c.}$$

At 0° and 760 mm., 1 equivalent (1 g.) of hydrogen occupies 22,400/2 c.c. = 11,200 c.c., and one equivalent of chlorine (35.46 g.) occupies the same volume. Thus

96,504 coulombs will liberate 22,400 c.c. of gas from HCl. The number of coulombs liberating 37.1 c.c. was, therefore,

$$96{,}504 \times \frac{37.1}{22{,}400} = 159.83 \text{ coulombs.}$$

Since about 160 coulombs passed through the solution in ten minutes, or 600 seconds, the amperage was 160/600 = 0.27 amperes.

Example 33. A current passing for 10 minutes through dilute sulphuric acid liberated 63 c.c. of gas at 0° and 760 mm. What number of coulombs was used, and what was the average amperage of the current?

At 0° and 760 mm., 1 equivalent of hydrogen occupies 22,400/2 c.c. = 11,200 c.c., and one equivalent of oxygen (8 g.) occupies 22,400/4 = 5600 c.c. Total from 96,504 coulombs 16,800 c.c. The number of coulombs liberating 63 c.c. is, therefore, $96{,}504 \times \frac{63}{16{,}800} = 361.8$ coulombs. The time was 600 seconds, so that the amperage was 362/600 = 0.6 amperes.

Example 34. An incandescent lamp carrying 50 watts on a 110 volt circuit (the lamp commonly employed for lighting rooms) is placed in series with an electrolytic cell containing dilute hydrochloric acid, saturated with chlorine. What volume of gas at 0° and 760 mm. will be liberated in 15 minutes?

110 × No. amperes = 50. Hence the amperage is 50/110 = 0.45 amperes. Now 0.45 amperes for 15 × 60 seconds (900 seconds) is equal to a total of 900 × 0.45 coulombs = 405 coulombs. Also 96,504 coulombs gives 22,400 c.c. Hence, 405 coulombs will give $22{,}400 \times \frac{405}{96{,}504}$ = 94 c.c. at 0° and 760 mm.

PROBLEMS.

217. A current is passed for 6 minutes through dilute hydriodic acid and liberates 36 c.c. of gas at 16° and 763 mm. What number of coulombs were used, and what was the average amperage of the current? *Ans.* 294.28; 0.817.

218. A current was passed through dilute sulphuric acid for 8.5 minutes and liberated 61 c.c. of gas at 0° and 760 mm. What number of coulombs were used, and what was the amperage of the current? *Ans.* 350.5; 0687.

219. A current passing for 18 minutes through dilute sulphuric acid liberated 101 c.c. of gas at 0° and 760 mm. What number of coulombs was used and what was the average amperage of the current? *Ans.* 580.4; 0.537.

220. Same data and questions as in **219**, except that dilute orthophosphoric acid was used. *Ans.* 580.4; 0.537.

221. A 50 watt, 110 volt incandescent lamp is placed in series with a cell containing dilute sulphuric acid. What volume of gas at 10° and 740 mm. will be liberated in 12 minutes? *Ans.* 60.028 c.c.

222. An incandescent lamp, on a 110 volt circuit, was placed in series with dilute hydrochloric acid, and in 5 minutes, 65 c.c. of gas were liberated. How many watts did the lamp carry? *Ans.* 102.72.

223. A 1.3 ampere current passes through an electrolytic cell containing dilute cupric sulphate solution. How much copper will be liberated in ten minutes? *Ans.* 0.2568 g.

224. An electrolytic cell contains dilute cupric sulphate solution, and is provided with copper electrodes the area of each of which is 900 sq. cm. With a 2.5 ampere current traversing the cell, what weight of copper will be deposited on one square centimeter of the cathode in one hour? If the anode contains 3 pounds (avoird.) of copper, what length of time will be required for the ionization of the whole anode? *Ans.* 0.0033 g.; 19 days 2 hours 10 minutes 48 seconds.

225. Calculate the time required for 0.6 amperes to deposit 100 g. of copper, from a copper sulphate solution. *Ans.* 141 hours 49 minutes.

226. A certain current of electricity ran 10 min. and deposited 655 mg. of silver. What was the amperage? *Ans.* 0.9768.

227. What would be the volume of hydrogen set free at 740 mm. and 20° C. from a dilute solution of sulphuric acid, if the current in **226** ran 18 min. through a hydrogen voltameter? *Ans.* 138.02 c.c.

Specific Conductivity. The specific resistance is the resistance in ohms of a cube of the substance with each edge 1 cm. long. The reciprocal of this is the specific conductivity. The unit is called the reciprocal ohm (r.o.) and is the conductivity of a 1 cm. cube with a resistance of 1 ohm. The specific conductivity is the current in amperes which flows through a 1 cm. cube when a difference in potential of 1 volt is applied to two opposite faces.

Example 35. If a solution 1 decimeter in cross section and 2.5 cm. long, with a difference in potential of 5 volts between the electrodes, carries 3 amperes, what is the specific conductivity of the solution?

The cross section is 10×10 sq. cm. $= 100$ sq. cm. With 5 volts for 2.5 cm., the voltage to force the same current through a layer 1 cm. thick would be $2.5/5 = 0.5$ volts. Hence 1 volt would give 6 amperes. The 6 amperes, however, are using 100 sq. cm. For 1 sq. cm. the amperage is $6/100 = 0.06$ amperes = sp. conductivity (r.o.)

Equivalent Conductivity. The equivalent conductivity is the number of amperes (or reciprocal ohms) passing through a solution containing one equivalent weight of the substance, arranged so that the electrodes are 1 cm. apart, and of area sufficient to include the whole of the solution between the electrodes.

Λ = specific conductivity $\times$ 1000 $\times$ No. liters containing one equivalent.

The **degree of ionization** (α) at a given dilution is the ratio of the equivalent conductivity at the given dilution to that at infinite dilution, *i.e.*, at a dilution beyond which no increase in conductivity occurs: $\alpha = \Lambda/\Lambda_\infty$.

The equivalent conductivity at infinite dilution (complete ionization) is the sum of the conductivities (mobilities) of the equivalent weights of the ions present.

Thus, for KCl, the concentration in gram-equivalents per liter, and the conductivities of one gram-equivalent are as follows:

Concn. (N).	Λ.	Concn. (N).	Λ
1	98.2	0.001	127.6
0.1	111.9	0.0001	129.5
0.01	122.5	$1/\infty$	131.2

The value at infinite dilution is obtained by extrapolation.

Velocity of Migration (Mobility) of Ions. The conductivity of a solution of an ionogen depends on three factors. (1) The number of ions between the electrodes, (2) the valence (no. of charges) of each ion (a bivalent ion, *e.g.*, Cu^{++}, carries twice as much electricity), (3) the velocity with which the ions move. In KCl solution, the number of positive and negative ions are equal, and the valences are also equal. The velocity of migration of K^+ and of Cl^- (unit, velocity in cm. per sec.) are different, and can be observed. When the relative velocities of K^+ and Cl^- have been observed, the value of the conductivity at infinite dilution (where, in this case, the numbers of K^+ and Cl^-, and the valences are alike) can be divided between the ions, and the ionic velocities can thus be stated in the same unit as the conductivity. The velocities (18 and 25°) on this scale, are as follows:

Ion.	18°.	25°.	Ion.	18°.	25°.
K.....	64.6	74.5	Cl.....	65.5	75.5
Na.....	43.5	50.9	NO_3.....	61.7	70.6
NH_4.....	64.5	74.5	$CH_3.COO$..	34.6	40.8
Ag.....	54.3	63.5	$\frac{1}{2}$ SO_4.....	68	79
$\frac{1}{2}$ Ba.....	55	65	OH.....	172	192
$\frac{1}{2}$ Ca.....	51	60	.....	.....	.....
H.....	314	347	.....	.....	.....

The most speedy ion is H^+, and the next fastest is OH^-. It will be seen that K^+ 64.67 + Cl^- 65.46 = 130.11, close to the observed value at infinite dilution (131.2).

Example 36. What is the degree of ionization of KCl in N and in 0.01 N solutions (p. 59)? In N solution it is 98.2/131.2 = 0.75 = 75 per cent. In 0.01 N solution it is 122.5/131.2 = 0.93 = 93 per cent. The values obtained in this way are more accurate for weak electrolytes than for strong electrolytes like KCl.

Example 37. What is the degree of ionization of ammonium chloride in N solution and in 0.01 N solution? The conductivities at 18° are 90.7, and 114.2, and, at ∞ dilution, 120.9. The degree of ionization is, therefore, N solution 90.7/120.9 = 0.75 = 75 per cent, 0.01 N solution 114.2/120.9 = 0.94 = 94 per cent.

PROBLEMS.

228. Tenth normal potassium chloride has specific conductivity of 0.01287 r.o. at 25° C., what is the resistance of a square column of this solution 8 cm. long and 2 cm. in width at 25°? *Ans.* 155.4 ohms.

229. What is the equivalent conductivity at 18° of $N/50$ potassium chloride, if its specific conductivity is 0.002397? *Ans.* 119.85 r.o.

230. If the equivalent conductivity of potassium chloride is 131.2 at infinite dilution at 18° C., calculate the degree of dissociation of the $N/50$ solution in **229.** *Ans.* 91 per cent.

231. (*a*) What is the equivalent conductivity at 18° of 0.9 N hydrochloric acid (α = 0.78)? (*b*) What is the equivalent conductivity at 18° of $N/64$ calcium hydroxide (α = 0.9)? *Ans.* (*a*) 296 r.o., (*b*) 200.7 r.o.

232. (*a*) Calculate the specific conductivity at 18° of 0.1 N acetic acid (α = 0.013). (*b*) Calculate the specific conductivity at 18° of 0.1 N sulphuric acid (α = 0.61). *Ans.* (*a*) 0.0_3453 r.o., (*b*) 0.0233.

233. The specific conductivity of 0.1 N hydrochloric acid = 0.03532 r.o. Calculate α. *Ans.* 0.93.

234. The specific conductivity at 18° of $N/64$ calcium hydroxide = 0.00319 r.o. Calculate α. *Ans.* 0.91.

235. For water at 18°, $H^+ \times OH^- = 1.2 \times 10^{-14}$. Calculate the specific conductivity of this water. *Ans.* 5.346×10^{-8} r.o.

236. Calculate the degree of dissociation of 0.15 molar hydriodic acid at 25°, if the equivalent conductance of iodide-ion is 389.5, and the conductance at infinite dilution for the iodide-ion is 440. *Ans.* 88.5 per cent.

237. The mobility of K^+ at infinite dilution is 64.6; of NO_3^- is 61.7. What is the degree of dissociation of $N/20$ potassium nitrate at 18°, if its equivalent conductivity is 109.86? *Ans.* 87 per cent.

238. Using the ionic mobilities, in above table (p. 60), calculate the value at 18° of the conductivity at infinite dilution of one equivalent of every possible acid, base, or salt. *Ans.* KCl 130.1; KNO_3 126.3; KCO_2CH_3 99.2; K_2SO_4 132.6; KOH 236.6; NaCl 109; $NaNO_3$ 105.2; $NaCO_2CH_3$ 78.1; Na_2SO_4 111.5; NaOH 215.5; NH_4Cl 130; NH_4NO_3 126.7; $NH_4CO_2CH_3$ 99.1; $(NH_4)_2SO_4$ 132.8; NH_4OH 236.5; AgCl 119.8; $AgNO_3$ 116; $AgCO_2CH_3$ 88.9; Ag_2SO_4 122.3; AgOH 226.3; $BaCl_2$ 120.5; $Ba(NO_3)_2$ 116.7; $Ba(CO_2CH_3)_2$ 89.6; $BaSO_4$ 123; $Ba(OH)_2$ 227; $CaCl_2$ 116.5; $Ca(NO_3)_2$ 112.7; $Ca(CO_2CH_3)_2$ 85.6; $CaSO_4$ 119; $Ca(OH)_2$ 223; HCl 379.5; HNO_3 375.7; HCO_2CH_3 348.6; H_2SO_4 382; H_2O 486.

239. Using the values obtained in the preceding problem, at 18°, calculate the degrees of dissociation of the following materials, the equivalent conductivity being given in brackets: $N/2$ hydrochloric acid (327); $N/100$ acetic acid (14.3); N potassium hydroxide (184); $N/100$ ammonium hydroxide (13.2); $N/500$ silver nitrate (110.03). *Ans.* 86.19 per cent; 4.1 per cent; 77.7 per cent; 5.58 per cent; 94.85 per cent.

240. At 107–8°, in acetic acid, the molecular weight of HBO_2 is 38.3 instead of 44. What is its degree of dissociation? (Nasini and Ageno, C.A., **4** (1910), 723.) *Ans.* 14.88 per cent.

241. If V is the volume of solution containing one gram-mole of sodium thiocyanate at the temperatures given, calculate from the conductivities below the degrees of dissociation for 0.25 molar sodium thiocyanate, assuming complete dissociation at $M/2048$ ($V = 2048$):

Temp.	0°	15°	25°	35°
For $V = 4$	46.79	69.00	84.36	102.5
For $V = 2048$	58.10	86.22	127.80	130.6

How does the conductivity change with rise in temperature? How does the degree of dissociation change with rise in temperature? (Jones and Watkins, Jour. Am. Chem. Soc., **36** (1915), 2626.) *Ans.* 0° 80.53 per cent; 15° 80.03; 25° 78.26 per cent; 35° 78.48.

242. From the data in the foregoing problem, calculate the specific conductivity of 0.25 molar sodium thiocyanate at 25°. *Ans.* 0.021 r.o.

243. Propionic acid, $HC_3H_5O_2$, is a monobasic acid. A 0.1 *N* solution in water has a specific conductivity of 3.97×10^{-4} r.o. The conductivity at infinite dilution 0.349 r.o. Calculate the OH^- concentration of this solution. *Ans.* 1.09×10^{-11} at 25°.

244. (*a*) A saturated solution of silver acetate contains 0.059 moles per liter, of which 0.72 is ionized. Calculate the solubility product. *Ans.* 1.80×10^{-3}. (*b*) What concentration of acetate ion is necessary to reduce the concentration of Ag^+ to 0.001 mole per liter. *Ans.* 1.80 molar.

Degrees of Dissociation by Boiling-Point and Freezing-Point Methods. Electrical conductivities can be measured much more accurately than can elevations in boiling-point (p. 38) and depressions in freezing-points (p. 39). Still, by the latter methods, rough estimates of degrees of ionization can be obtained. The boiling-point, of course, gives values for dissociation at the temperatures of boiling, over 100° for water, and may be materially different from those found by conductivity at 18° or 25°. The freezing-point temperatures give values closer to those found at 18° or 25° [334–338, *213–216*].

Boiling-Point. Example 38. A normal solution of potassium chloride boils at a temperature 0.92° above that of water. What is the degree of dissociation? For one molecular weight of a non-dissociated substance in 1000 g. of water the b.-p. elevation is 0.52°. Here the substance gives only two ions. The excess depression 0.40° therefore is due to the extra ions. The result indicates that 0.40/0.52 is dissociated, or 0.77 or 77 per cent.

If the substance had been 2 N barium nitrate, giving an elevation in the b.-p. of 1.12, we must note that this gives three ions. Subtracting 0.52, the elevation due to dissociation is 0.60, caused by two ions. The number of molecules dissociated is therefore 0.30. This is 0.30/0.52 of the whole or 0.58 or 58 per cent.

PROBLEMS.

245. If 2 N cupric sulphate solution is 22 per cent dissociated at its boiling-point in water, what elevation in the b.-p. would it give? *Ans.* 0.634°.

246. What is the degree of dissociation of zinc sulphate, if 5 g. of it dissolved in 125 g. of water produce a lowering of 0.603° in the f.-p.? What is the molecular concentration of each of the three substances present in this solution? One mole of a non-ionized substance, in 1000 c.c. of water, lowers the freezing-point to −1.86°. *Ans.* 30.8 per cent; Zn^{++} 0.0763; SO_4 0.0763; $ZnSO_4$ 0.1715.

247. What will be the approximate b.-p. of a solution of common salt, saturated at 100°? Assume that the solute is 50 per cent dissociated. *Ans.* 105.2°.

248. In a decinormal solution, potassium chloride is 86 per cent dissociated. What is the freezing-point of this solution? *Ans.* −0.346°.

Dissociation Constants. If α is the degree of dissociation of a binary electrolyte, and the total concentration in moles per liter is given, the molar concentration of each ion is $\alpha \times$ total molar concentration, and that of the undissociated electrolyte is $(1 - \alpha) \times$ total molar concentration. According to the law of concentration (mass-action), therefore, the dissociation constant K has the value:

$$K = \frac{(\alpha \times \text{molar concn.})^2}{(1 - \alpha) \times \text{molar concn.}}$$

$$= \frac{\alpha^2 \times \text{molar concn.}}{(1 - \alpha)} = \frac{\alpha^2}{(1 - \alpha)\, v},$$

where v is the volume in liters containing one mole. This formula is reasonably accurate only for weak electrolytes. With strong electrolytes, K does not give constant values at different dilutions.

The conductivities may be used directly, for $\alpha = \frac{\Lambda}{\Lambda_\infty}$. Hence:

$$K = \frac{(\Lambda/\Lambda_\infty)^2}{(1 - \Lambda/\Lambda_\infty)\, v} = \frac{\Lambda^2}{\Lambda_\infty\,(\Lambda_\infty - \Lambda)\, v}.$$

For a substance, like $Ca(OH)_2$, giving three ions

$$K = \frac{(\alpha \times \text{molar concn.})^3}{(1 - \alpha) \times \text{molar concn.}}$$
$$= \frac{\alpha^3 \times \text{molar concn.}^2}{1 - \alpha} = \frac{\alpha^3}{(1 - \alpha)\, v^2}.$$

Example 39. Find the dissociation constants for the following substances, the fraction ionized being given for 0.1 N solutions: Acetic acid (0.013), carbonic acid ($H.HCO_3$ 0.0017), water (0.0_61), ammonium hydroxide (0.013).

Acetic acid $K = \frac{(0.013)^2}{(1 - 0.013)\, 10} = \frac{0.000169}{0.987 \times 10} = 1.7 \times 10^{-5}$.

$H.HCO_3$, $K = \frac{(0.0017)^2}{(1 - 0.0017)\, 10} = 2.9 \times 10^{-7}$.

H_2O, $K = \frac{(0.0_61)^2}{(1 - 0.0_61)\, 10} = \frac{0.0_{13}1}{(0.9_7)\, 10} = 1.0 \times 10^{-14}$.

NH_4OH, $K = \frac{(0.013)^2}{(1 - 0.013)\, 10} = 1.7 \times 10^{-5}$.

PROBLEM.

249. Find the dissociation constants of the following substances, the fraction ionized in 0.1 N solution being given: hydrogen sulphide (H.HS 0.0007); hydrocyanic acid (0.0001); hypochlorous acid (0.0002). *Ans.* 0.0_5245; 0.0_61; 0.0_64.

Example 40. Find the dissociation constant for $Ca(OH)_2$ ($N/64$, the fraction dissociated is 0.90). $K = \frac{Ca^{++} \times OH^{-2}}{Ca(OH)_2}$, where $[OH^-]$ is the *total* OH^- concentration. All dissociation constants are calculated on the basis of molar (not normal) solutions. Hence $N/64$ $Ca(OH)_2$ equals $M/128$ $Ca(OH)_2$, or 0.0078 molar. Since the base is 0.9 dissociated, the concentration of Ca^{++} $[Ca^{++}]$ is $0.0078 \times 0.9 = 0.00702$. Since each molecule gives $2OH^-$, $[OH^-]$ has the value $2 \times 0.00702 = 0.01404$. The value of $[Ca(OH)_2]$, undissociated, is $0.1 \times 0.0078 = 0.00078$. Hence:

$$K = \frac{0.00702 \times (0.01404)^2}{0.00078} = 9 \times (0.01404)^2 = 0.001774$$

or 1.774×10^{-3}.

PROBLEMS.

250. Calculate the ionization constant of hydrochloric acid for the following concentrations: N HCl, $\alpha = 0.788$; $N/2$ HCl, $\alpha = 0.85$; 0.1 N HCl, $\alpha = 0.922$. *Ans.* $K = 2.797$, 2.048, 1.06.

251. Formic acid HCOOH at a dilution of 4.6 g. per liter gives a specific conductivity of 1.7×10^{-3} r.o. Calculate the ionization constant. Conductivity at infinite dilution is 376 r.o. *Ans.* 0.0021.

252. For acetic acid $K = 1.8 \times 10^{-5}$. Calculate α for $N/2$ solution. *Ans.* 0.00598.

253. Calculate the concentration of H^+ in 0.1 N hydrocyanic acid. $K = 7 \times 10^{-10}$. *Ans.* 8.36×10^{-6}.

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CHAPTER VIII.

SOLUBILITY PRODUCT CONSTANT; EFFECT OF COMMON ION; HYDROLYSIS; NEUTRALIZATION; COMPLEX COMPOUNDS; SENSITIVENESS OF INDICATORS.

Solubility Product Constant. This conception is applied mainly to rather insoluble substances. When a solid ionogen is in contact with its saturated solution, the concentration of undissociated molecules is constant [697–700, 710–716, *466–472*, *478–484*, St. 139–147]. Hence, the product of the concentrations of the ions is constant. For a binary salt, the formula is:

$[A^+] \times [B^-]$ = Sol'ty product constant, where $[A^+]$ and $[B^-]$ represent the concentrations in gram-molecules per liter of the two ions. For a more complex salt, such as CaF_2, the formula is:

$[Ca^{++}] \times [2F^-]^2$ = Sol'ty product constant. Here each ionized molecule gives a double concentration of $[F^-] = [2F^-]$.

For salts, like silver chloride, which are highly ionized, the undissociated molecules are so few that they may be ignored, practically all the dissolved molecules being ionized. In such a case, the concentration of each ion is identical with the concentration of the dissolved salt. In cases where the ionization is incomplete, the degree of ionization will be given.

Example 41. A saturated solution of silver acetate contains 0.059 moles per liter. Degree of ionization (α) is 0.72. Calculate the solubility product constant.

Of the 0.059, 72 per cent is ionized, *i.e.*, $0.059 \times 72 \div 100 = 0.0425$ ionized. This is the molar concentration of each ion. The ion product constant is, therefore, $0.0425 \times 00425 = 1.8 \times 10^{-3}$.

Example 42. The solubility of calcium fluoride in water is 0.0016 g. per 100 c.c. Calculate the solubility product constant. The molecular weight of CaF_2 is 78, and the concentration must first be expressed in moles per liter:

$$0.0016 : 100 : : x \times 78 : 1000$$
$$x = 1.6/7800 = 0.000205$$

Solubility product $= 0.000205 \times (2 \times 0.000205)^2 = 5.33 \times 10^{-11}$. Here complete dissociation is assumed.

Solubility Product, with Excess of One Ion. When excess of one ion, due to the presence of a more soluble ionogen, having one ion in common with the insoluble ionogen, is present, the concentration of the other ion can be calculated, and the solubility of an insoluble ionogen under such conditions can be determined.

Example 43. If, to a saturated solution of silver acetate (sol'ty 0.059 M/L), there be added sufficient sodium acetate to give an additional concentration of acetate-ion of 0.035 per liter, what will be the concentration of the silver-ion and of silver acetate? The silver acetate is 72 per cent ionized, giving a molar concentration of each ion of 0.0425 moles per liter (example above, p. 67). The solubility product was 1.8×10^{-3}. Here,

$$1.8 \times 10^{-3} = x\,(x + 0.035). \quad x = 0.0284.$$

The molar solubility of silver acetate will be 0.0284 plus undissociated molecules, which, in presence of the solid, will be the same as before, or 28 per cent of the 0.059 $= 0.0165$. Total molar solubility 0.0449 per liter.

Example 44. What concentration of acetate-ion is necessary to reduce the concentration of silver-ion from saturated silver acetate solution to 0.001 moles per liter?

$$1.8 \times 10^{-3} = 0.001 \times x. \quad x = 1.8 \text{ moles per liter.}$$

Example 45. Calculate the molar concentration of OH^- in a solution containing 10 c.c. of N ammonium hydroxide and 25 c.c. of 0.025 N ammonium chloride, diluted to 100 c.c. Assume the ammonium chloride completely ionized.

The ionization constant K of ammonium hydroxide is 0.000018, and a 0.1 N solution is 1.3 per cent dissociated. Hence, 0.013×0.1 or 0.0013 is the molar concentration of NH_4^+ and of OH^- in *pure* 0.1 N ammonium hydroxide solution. Since the solution also contains 0.006 N ammonium chloride, 100 per cent dissociated, the total NH_4^+ concentration is $0.006 + 0.0013$, provided no NH_4^+ is used in forming NH_4OH molecules. However, some NH_4OH molecules are formed. The concentration of OH^- is thus reduced from 0.0013 to x, and the concentration of NH_4^+ from the NH_4OH alone is also x. Hence:

$$0.000018 = \frac{(0.006 + x)\, x}{(0.1 - x)},$$

or $$0.006\, x + x^2 = 0.0000018 - 0.000018\, x.$$

Now, disregarding $0.000018\, x$, which is a very small quantity, we have: $(x + 0.003)^2 = 0.0000018$,

or $x - 0.003 = 0.00328$, hence $x = 2.8 \times 10^{-4}$.

PROBLEMS.

254. The solubility product of $Ag_3PO_4 = 1.8 \times 10^{-18}$. That of $Ag_2CrO_4 = 1.7 \times 10^{-12}$. Which, in saturated solution, gives the lower concentration of Ag^+? *Ans.* Ag^+ from $Ag_3PO_4 = 4.81 \times 10^{-5}$, from Ag_2CrO_4 1.50×10^{-4}.

255. The solubility product of $CuS = 8.5 \times 10^{-45}$. That of $Bi_2S_3 = 2.6 \times 10^{-91}$. Which, in saturated solution, gives the lower concentration of sulphide ion? *Ans.* From $CuS = 9.22 \times 10^{-23}$, from $Bi_2S_3 = 8.97 \times 10^{-19}$.

256. $CaSO_4$ is soluble to the extent of 0.015 moles per liter; $SrSO_4$ is soluble to the extent of 0.0006 moles per liter. What concentration of Ca^{++} would be required to precipitate $CaSO_4$ from a saturated $SrSO_4$ solution? *Ans.* 0.375 moles per liter.

257. What concentration of Cl^- must be present in order that AgCl shall precipitate from a saturated Ag_2S solution? AgCl is soluble to the extent of 0.00016 g. per 100. c.c. H_2O, while $K_{s.p.}$ of $Ag_2S = 3.2 \times 10^{-50}$. *Ans.* 3.0×10^6 moles per liter.

258. A saturated solution of SrF_2 contains 0.00093 moles per liter. A saturated solution of $SrCrO_4$ contains 0.006 moles per liter. If to a solution, normal with respect to F^- and $CrO_4^=$, $SrCl_2$ were added, what precipitate would appear first, and what would be the ratio of F^- to $CrO_4^=$ in the solution when both precipitates finally appear? *Ans.* SrF_2 first. $(F^-)^2/CrO_4^= = 8.9 \times 10^{-5}$.

259. A certain solution contains 0.0012 gram-equivalents per liter of Ba^{++} together with some Ag^+. $Na_2C_2O_4$ is added, together with sufficient acid to allow an almost complete precipitation of the Ag^+ as $Ag_2C_2O_4$, but also sufficient to prevent any BaC_2O_4 from precipitating. Between what limits does the concentration of C_2O_4 lie? Solubility product of $Ag_2C_2O_4 = 1.3 \times 10^{-11}$. Solubility product of $BaC_2O_4 = 3.5 \times 10^{-7}$. *Ans.* Between 1.47×10^{-4} and 5.8×10^{-4}.

260. AgBr is soluble to the extent of 0.0_65916 moles per liter. AgCNS is soluble to the extent of 0.0_68426 moles per liter. In a solution 0.1 *N* with respect to both Br^- and CNS^-, what are the limits of concentration of Ag^- that may be present, such that AgBr will just begin to precipitate but AgCNS will not? *Ans.* Between 3.5×10^{-12} and 7.1×10^{-12}.

261. $K_{s.p.}$ of $AgCNS = 7.1 \times 10^{-13}$. The molar solubility of $AgBr = 5.916 \times 10^{-8}$ moles per 100 c.c of solution. When equal volumes of saturated solutions of AgBr and AgCNS are mixed, what precipitate, if any, will result? *Ans.* None.

262. On mixing 10 c.c. of saturated BaF_2 (sol. product const. 1.7×10^{-6}) solution with 90 c.c. of saturated $BaSO_4$ (sol. product const. 1.2×10^{-10}) solution what precipitate, if any, will result? *Ans.* Barium sulphate.

263. Equal volumes of clear saturated solutions of AgCl and TlI are mixed. What salt or salts, if any, will precipitate? *Ans.* AgI.

264. Equal volumes of clear saturated solutions of $MgNH_4PO_4$ (sol. prod. const. 2.5×10^{-13}) and of Ag_2CO_3 (sol. prod. const. 6.0×10^{-12}) are mixed. What salt or salts, if any, will precipitate? *Ans.* Silver phosphate.

265. A solution containing 0.1 M/L Ca^{++} is mixed with an equal volume of 0.1 M $Na_2C_2O_4$ (0.9 ionized in final solution). What conc. H^+ is necessary to prevent CaC_2O_4 (sol. prod. const. 2.5×10^{-9}) from precipitating? *Ans.* 1.308 M/L.

266. The concentration of $H^+ = 1.077 \times 10^{-5}$. To how many c.c. would 3 c.c. of 6 N acetic acid have to be diluted to give this concentration of hydrogen-ion, without adding any sodium acetate? *Ans.* 1,045,900 c.c.

267. The solubility product constant of silver chloride is 1.12×10^{-10}. If AgOH has fourteen times the molar solubility of AgCl, calculate the specific conductivity of its saturated solution at 18°. *Ans.* 3.53×10^{-5} r.o.

268. A saturated solution of magnesium hydroxide contains 0.001 g. per 100 c.c. If 0.1 N ammonium hydroxide be added to an equal volume of 0.1 M magnesium sulphate, what concentration of NH_4^+ must be present to prevent the precipitation of $Mg(OH)_2$? α of $MgSO_4$ in final solution is 0.5. *Ans.* 0.0285 M NH_4^+.

269. Calcium fluoride is soluble at 18° to the extent of 0.0004 N and calcium carbonate to the extent of 0.0002 N. If, to a solution 0.1 M with respect to F^- and $CO_3^=$, calcium chloride is added, which precipitate will first appear? What will be the ratio of F^- to $CO_3^=$, when both precipitates have formed? *Ans.* CaF_2; $[F^-]^2/[CO_3^=] = 3.2 \times 10^{-3}$.

270. The solubility of calcium sulphate is 0.015 M. The solubility product of barium sulphate is 1.2×10^{-10}. Could calcium sulphate be precipitated by adding Ca^{++} to a saturated barium sulphate solution? *Ans.* $[Ca^{++}]$ required = 20.54 M.

271. From the data given in **173,** Chap. V, calculate the solubility product of silver iodate, assuming complete dissociation in the saturated solution. *Ans.* 0.000138.

272. Kendall (Phil. Mag., **23,** 958) gives the solubility of calcite at 25° C., as 0.01433 g. per liter; of aragonite at 25° C., as 0.01528 g. per liter. Calculate the solubility products of the two forms of

calcium carbonate, and interpret. *Ans.* Calcite 2.05×10^{-8}, aragonite 2.335×10^{-8}.

273. Van Rossem (Chem. Weekblad, **9,** 203) gives the solubility of silver chloride at 18° as 1.020×10^{-5} g. equivalent per liter, and at 25°, to be 1.429×10^{-5}. Find its solubility products at these two temperatures. *Ans.* 18° 1.04×10^{-10}; 25° 2.04×10^{-10}.

274. What is the concentration of chloride-ion in a solution of $N/100$ silver nitrate saturated at 25° with silver chloride? Assume dissociation of $AgNO_3 = 0.92$. *Ans.* 1.02×10^{-5}.

275. Hevesy and Pareth (Zeit. Anorg. Chem., **82,** 323) give the solubility of lead chromate at 25° as 1.2×10^{-5} g. per liter. What is its solubility product? *Ans.* 1.37×10^{-15}.

276. The same writers give the solubility of lead sulphide at 25° in distilled water as 3×10^{-4} g. per liter. If the solubility in water saturated with hydrogen sulphide is 1.5×10^{-4} g., what is the total concentration of free sulphide ion in the mixture? *Ans.* 2.51×10^{-8} *M*.

277. Sackur & Fritzmann (Z. Elektrochemie, **15,** 842–6) state that the molar solubility of manganous hydroxide is 2.15×10^{-5} g. moles per liter. What is its solubility product? *Ans.* 3.5×10^{-14}.

278. If at 25° C. thallous iodide dissolves to the extent of 1.76×10^{-4} moles per liter, calculate its solubility product. *Ans.* 3.10×10^{-8}.

279. According to Walden (Chem. Abstracts, **7** (1913) 3564) 3.82 liters of water are required to dissolve 1 mole of tetramethylammonium iodide at 25° C., and the degree of dissociation of the saturated solution is 68 per cent. For saturated potassium iodide the degree of dissociation at 25° is 42.3 per cent, and a liter of water dissolves about 1470 g. of the salt. Calculate the approximate result, if 100 c.c. of water were first saturated with tetramethylammonium iodide and with potassium iodide, on the assumption of no volume change in the solution, and that the mass action law holds. *Ans.* 0.97 moles of N $(CH_3)_4I$ ppd.

280. 2.7 g. of sodium acetate ($NaC_2H_3O_2,3H_2O$) is dissolved in 1 l. of 0.1 *N* acetic acid (ionization constant 18×10^{-6}). What is the concentration of hydrogen-ion in this solution, if the sodium acetate is 0.9 dissociated? (See A.A. Noyes, Jour. Amer. Chem. Soc., **32** (1910), 822.) *Ans.* $H^+ = 0.00001$ *M*.

Hydrolysis. Water gives a very small concentration of $[H^+]$ and $[OH^-]$. As the concentration of the water is constant, the product of the concentrations of the two ions at 18° is constant: $[H^+] \times [OH^-] = 0.8 \times 10^{-14}$. A salt which could be formed from an active base and an active acid is not affected by water at room temperature, because the concentrations of H^+ and OH^- are too small to produce any combination with the radicals. Thus $Na^+ + Cl^- + H^+ + OH^- \leftarrow NaOH + HCl$ gives none of the acid or the base. When, however, the acid or the base is weak, some combination to form undissociated molecules occurs. Thus, potassium cyanide, $K^+ + CN^- + H^+ + OH^- \rightarrow HCN + K^+ + OH^-$, gives a little undissociated hydrocyanic acid (weak acid), but KOH is highly dissociated, so that an excess of OH^- remains and the solution is alkaline. This sort of action is called hydrolysis, and usually the action increases with dilution. Similarly, aluminium chloride solution shows an acid reaction, because aluminium hydroxide is a very weak base: $Al^{+++} + 3Cl^- + 3H^+ + 3OH^- \rightarrow Al(OH)_3 + 3Cl^- + 3H^+$. Hydrolysis, however, usually affects only a small fraction of the salt, unless one product is insoluble and thus causes further displacement of the equilibrium. Thus, in a molar solution of KCN, the proportion of the salt which is hydrolyzed is only 0.3 per cent. Even in a very dilute solution of aluminium chloride, which is only 0.001 *N*, the hydrolysis at 25° reaches only 4.5 per cent [398, 418, 646, 814, *271*, *437*, *592*, St. 178–188].

For the case where the **acid is weak** and the base active:

$$\text{Hydrolytic constant} = \frac{K_{\text{acid}}}{K_{\text{HOH}}} = \frac{[\text{Salt}]}{[\text{Free acid}] \times [\text{Free base}]}.$$

When the **base is weak**, and the acid active;

$$\text{Hydrolytic constant} = \frac{K_{\text{base}}}{K_{\text{HOH}}} = \frac{[\text{Salt}]}{[\text{Free acid}] \times [\text{Free base}]}.$$

Example 46. The ionization constant of hydrocyanic acid K_{HNC} is 7.2×10^{-10}, and that of water K_{HOH} at 18° is 0.8×10^{-14}. Calculate the per cent hydrolyzed for molar potassium cyanide solution. The concentrations of free acid and free base are equal, say x. The concentration of the remaining salt is $1 - x$. Hence:

$$\text{Hydrolytic constant} = \frac{7.2 \times 10^{-10}}{0.8 \times 10^{-14}} = \frac{1 - x}{x^2}.$$

$$90{,}000\,x^2 + x - 1 = 0. \quad x = 0.0033 \text{ or } 0.33 \text{ per cent.}$$

For decimolar potassium cyanide the equation is:

$$\frac{7.2 \times 10^{-10}}{0.8 \times 10^{-14}} = \frac{0.1 - x}{x^2}, \text{ where } x = 0.00105 \text{ or } \frac{0.00105}{0.1} \times 100$$

$= 1.05$ per cent in 0.1 M solution.

Example 47. Find the percentage hydrolysis at 25° of 0.1 M $NaNO_2$. Ionization constant of HNO_2, a weak acid, is 5×10^{-4}, of NaOH is 1. Of water at 25° 1.2×10^{-14}. $NaNO_2$ in 0.1 N solution is ionized about 84 per cent.

$$\frac{5 \times 10^{-4}}{1.2 \times 10^{-10}} = \frac{0.84\,(1 - x)}{x^2}, \text{ where } x = 4.5 \times 10^{-6}.$$

The percentage hydrolysis has one hundred times this value, or 4.5×10^{-4}.

PROBLEMS

281. According to Kullgren (Chem. Abstracts, **8** (1914), 608), zinc nitrate is hydrolyzed thus: $Zn(NO_3)_2 + H_2O \rightleftarrows ZnOHNO_3 + HNO_3$. At 100° C. the degree of hydrolysis of this salt in 1/64 molar solution is 0.00094 and the ionic product of water (100°) is 42×10^{-14}. Calculate the dissociation constant of the base ZnOH (NO_3). *Ans.* 3×10^{-5}.

282. Calculate the percentage hydrolysis of M, 0.1 M, and 0.01 M solutions of (*a*) $NaNO_2$ at 25°, and (*b*) KCN at 18°. *Ans.* (*a*) 0.00049 per cent, 0.0015, 0.0049, (*b*) 0.33 per cent, 1.05 per cent, 3.33 per cent.

283. Calculate the percentage hydrolysis of M, 0.1 M, and 0.01 M solutions of NH_4CN. *Ans.* 44.05 per cent for all three.

284. Calculate the concentration of OH^- in 0.1 M KCN and in 0.1 M $NaNO_2$ solutions. *Ans.* 0.00105 M/L; 1.56×10^{-6} M/L.

Complex Compounds. When ammonium hydroxide solution is added to a solution of a salt of silver, or to a silver salt which is not extremely insoluble, a solution containing the complex ion $Ag(NH_3)_2^+$ is formed. There is, of course, free dissolved ammonia in ammonium hydroxide solution. As this ion is not extremely stable, an excess of ammonia is required. Some silver-ion Ag^+ is also present. The formula

$$\frac{[NH_3]^2 \times [Ag^+]}{[(NH_3)_2\,Ag^+]} = K_{\text{Instability}}$$

defines the instability of the ion. The larger the constant, the greater the free Ag^+, and the greater the instability. The value of the constant at 25° is 6.8×10^{-8} [St. 216–230].

Example 48. What is the concentration of silver-ion in a 0.05 M solution of $Ag(NH_3)_2NO_3$? In such a solution the salt is ionized about 87 per cent. If x is the concentration of Ag^+, then 2 x is the concentration of free ammonia. The concentration of the complex ion is $0.05 \times 0.87 - x$. Thus

$$\frac{[NH_3]^2 \times [Ag^+]}{[(NH_3)_2Ag^+]} = \frac{(2\,x)^2 \times x}{0.05 \times 0.87 - x} = 6.8 \times 10^{-8}.$$

The x in the denominator is so small compared with $0.05 \times 0.87 = 0.0435$, that it may be omitted. Hence $4\,x^3 = 0.0435 \times 6.8 \times 10^{-8}$. $x = 0.0009 = [Ag^+]$.

Example 49. Could silver chloride be precipitated from the foregoing solution? The molar solubility of AgCl at 25° is 0.000014, and the solubility product constant, assuming complete ionization, is $(0.000014)^2 = 2 \times 10^{-10}$. If 1 c.c. of 0.1 *M* sodium chloride solution is added to 10 c.c. of 0.05 *M* ammonia-silver nitrate, the chloride is diluted 11 times, and is ionized about 87 per cent. Hence $[Cl^-] = 0.1 \times 1/11 \times 0.87 = 0.008$. The $[Ag(NH_3)_2^+]$ is $0.05 \times 10/11 \times 0.87 = 0.04$. Using the formula employed above $\frac{4x^3}{0.04} = 6.8 \times 10^{-8}$, where $x = 0.00089 = [Ag^+]$. Hence $Ag^+ \times Cl^- = 0.00089 \times 0.008 = 7 \times 10^{-6}$. As this value is larger than the solubility product constant of AgCl (2×10^{-10}), the salt is precipitated. Removal in this way of the free Ag^+ leads to further decomposition of the complex ion, and so considerable precipitation occurs.

Other Complex Compounds. The instability constants for cadmium-ammonia-ion and zinc-ammonia-ion are:

$$\frac{[Cd^{++}] \times [NH_3]^4}{[Cd(NH_3)_4^{++}]} = 1 \times 10^{-7}. \qquad \frac{[Zn^{++}] \times [NH_3]^4}{[Zn(NH_3)_4^{++}]} = 2.6 \times 10^{-10}.$$

Similarly:

$$\frac{[Ag^+] \times [CN^-]^2}{[Ag(CN)_2^-]} = 1 \times 10^{-21}. \qquad \frac{[Cu^+] \times [CN^-]^3}{[Cu(CN)_3^=]} = 0.5 \times 10^{-27}.$$

PROBLEMS.

285. Could silver bromide be precipitated as was silver chloride in the example above? Solubility of AgBr at 25° 0.0000006 *M*. Could silver iodide be precipitated (solubility 0.00000001 *M*)? *Ans.* Yes; yes.

286. If to $M/100$ $ZnSO_4$ ($\alpha = 1.00$) an equal volume of $3\,N$ NH_4OH is added (2/3 free NH_3), what concentration of $S^=$ would be required to precipitate ZnS? The solubility product constant of ZnS $= 1.2 \times 10^{-23}$. *Ans.* 0.9×10^{-11}.

287. If 3.40 g. of NH_3 gas is passed into 1000 c.c. of $N/10$ $AgNO_3$ solution, what concentration of Cl^- must be present to precipitate AgCl? Solubility product constant of AgCl $= 1.12 \times 10^{-10}$. *Ans.* $9.42 \times 10^{-8}\,M/L$.

Sensitiveness of Indicators. The question is, what molar concentration will just cause change in color of the indicator? The concentration of H^+ or of OH^- at which the indicator changes color must be given.

Example 50. What molar concentration of hydrocyanic acid will change methyl orange from yellow to reddish-orange? It is concn. $H^+ = 1 \times 10^{-4}$. The ionogen dissociates thus: $HNC \rightleftarrows H^+ + NC^-$, and its ionization constant is $7.2\ 10^{-10}$. The formula is:

$$\frac{[H^+] \times [NC^-]}{[HNC]} = \text{ionizn. const.}$$

$$\frac{1 \times 10^{-4} \times 1 \times 10^{-4}}{x - 1 \times 10^{-4}} = 7.2 \times 10^{-10}.$$

$7.2 \times 10^{-10}\,x - 7.2 \times 10^{-10} \times 1 \times 10^{-4} = (1 \times 10^{-4})^2 = 1 \times 10^{-8}$.
$7.2 \times 10^{-10}\,x - 7.2 \times 10^{-14} = 1 \times 10^{-8}$.
Now 7.2×10^{-14} is so small compared with 1×10^{-8} that the former may be neglected.

$$x = \frac{1 \times 10^{-8}}{7.2 \times 10^{-10}} = \frac{100}{7.2} = 13.9 \text{ molar.}$$

Example 51. What molar concn. of nitrous acid (ionization const. 5.0×10^{-4}) is required to turn methyl orange from yellow to reddish-orange?

$$\frac{[1 \times 10^{-4}] \times [1 \times 10^{-4}]}{x - 1 \times 10^{-4}]} = 5.0 \times 10^{-4}.$$

$$5 \times 10^{-4} x - 5 \times 10^{-4} \times 1 \times 10^{-4} = 1 \times 10^{-8}.$$
$$5 \times 10^{-4} x - 5 \times 10^{-8} = 1 \times 10^{-8}.$$
$$5 \times 10^{-4} x = 1 \times 10^{-8} \times 5 \times 10^{-8} = 6 \times 10^{-8}.$$

$$x = \frac{6 \times 10^{-8}}{5 \times 10^{-4}} = 1.2 \times 10^{-4} = 0.00012 \text{ moles per liter.}$$

Example 52. What is the percentage hydrolysis of sodium bicarbonate in 0.1 *M* solution?

$$\frac{5 \times 10^{-7}}{0.8 \times 10^{-14}} = \frac{0.1 - x}{x^2}$$

$$5 x^2 + 0.0000008 x - 0.00000008 = 0.$$

$x = 0.00013$, or $\frac{0.00013}{0.1} \times 100 = 0.0013$ per cent in 0.1 *M* solution.

PROBLEMS.

288. How much must solutions of (*a*) HNC, (*b*) H_2CO_3, (*c*) $HC_2H_3O_2$ be diluted to be "neutral" to methyl orange? The latter changes from yellow to reddish-orange at $C_{H+} = 1 \times 10^{-4}$. *Ans.* (*a*) 13.9 molar, (*b*) 0.00012 molar, (*c*) 0.000655.

289. Would *N*/10 aniline chloride be neutral to methyl orange? *N*/100? *N*/1000? *Ans.* Acid; neutral; neutral.

290. Phenolphthalein changes to pink when C_{OH^-} is increased to 1×10^{-6}. Would *M*/100 Na_2CO_3 be alkaline to this indicator? *M*/10,000? *M* $NaHCO_3$? *M*/100? *Ans.* Yes, yes; yes, yes.

291. (*a*) Pure water is acid to phenolphthalein. About how much NH_3 gas would it be necessary to add to 1000 c.c. to give an alkaline reaction towards this indicator? *Ans.* (*a*) 1.06×10^{-6} molar. (*b*) Approximately how much Na_2HPO_4? *Ans.* (*b*) 2.1×10^{-5} molar, or 0.00298 g. per liter.

292. (*a*) How much NaH_2PO_4 would it be necessary to add to 100 c.c. of water to give an acid reaction toward methyl orange? *Ans.* (*a*) 6 g. (*b*) Could sufficient NH_4Cl be added to give the same result? *Ans.* (*b*) No.

293. To what extent must 1 c.c. of tenth molar sodium hydrogen-oxalate be diluted to be no longer acid to methyl orange, assuming 100 per cent dissociation of the salt into sodium and hydrogen-oxalate ions? *Ans.* 3333.3 c.c.

294. To 30 c.c. of tenth molar sodium hydroxide are added a few drops of phenolphthalein. How much one-hundredth molar phosphoric acid must be added to make this solution acid? *Ans.* 66.67 c.c.

295. The ionization constant of ammonium hydroxide is 16×10^{-6}. Calculate the least concentration of this base necessary to turn methyl orange yellow, if the change occurs between $[H^+]\ 10^{-4}$ and 10^{-5}. *Ans.* 0.8×10^{-10} moles NH_4OH per liter.

296. Litmus turns red from red-violet at a hydrogen-ion concentration between 1×10^{-6} and 1×10^{-5}, and phenolphthalein turns red when H^+ falls below 1×10^{-9}. With the data given, which of the three indicators, litmus, methyl-orange or phenolphthalein should be used, in titrating ammonium hydroxide against $N/10$ sulphuric acid? *Ans.* Methyl-orange.

CHAPTER IX.

ELECTROMOTIVE FORCE; OXIDATION AND REDUCTION.

E.M.F. with Normal Ion Concentration. In a cell containing a metallic pole, immersed in a solution containing normal concentration of the corresponding metal-ion, the difference in potential between the pole and the liquid is shown in the following table. The charge (+ or −) preceding the value is the charge in the solution [786–800, *539–550*].

POTENTIAL IN VOLTS OF SOLUTIONS WITH N-ION CONCENTRATION IN CONTACT WITH METALS (E.-M. SERIES)

Mg	+1.3	Ni	−0.02?	Sb	−0.71?
Al	+1.0	Pb	−0.12	$Hg(Hg^{+})$	−0.99
Mn	+0.8	Sn (Sn^{++})	−0.14	Pd	−1.03?
Zn	+0.5	H	−0.24	Ag	−1.04
Fe (Fe^{++})	+0.2	As	−0.53	Pt	−1.10?
Cd	+0.16	Cu (Cu^{++})	−0.58	Au	−1.7?
Co	+0.05	Bi	−0.63?		

The potential of a cell, containing poles of different metals, each immersed in a solution as defined above, can be calculated from the table.

Example 50. If the metals are zinc and copper, the E.M.F. of the cell is $+0.5 - (-0.58) = 1.08$ volts. The two values are always subtracted, algebraically.

The values for **non-metals,** in volts, under the same conditions, are as follows:

I^- −0.78	Cl^- −1.64	HSO_4^- −2.9
Br^- −1.32	OH^- −1.96	
$O^=$ −1.36	$SO_4^=$ −2.2	

As before, the anode potential is supposed to work against the cathode potential and is subtracted from it.

Example 51. Thus, the cell with zinc and bromine-water, in presence of normal concentration of the respective ions, gives $+0.5 - (-1.32) = 1.82$ volts. Similarly, the cell in which bromine displaces iodine gives $-0.78 - (-1.32) = 0.54$ volts.

Values with Other Ionic Concentrations. When the same metal constitutes both poles, but the concentrations of the two solutions in respect to the corresponding metal-ion are different, the difference in potential at 18° can be calculated. Here the E.M.F. $= \frac{0.058}{\text{valence}} \log \frac{C^{I}}{C^{II}}$. The valence is that of the metal-ion, common logarithms are used, and C^{I} and C^{II} are the normal concentrations of the metal-ions in the two solutions.

Example 52. If the metal-ion is copper, and one solution is 10 N and the other 0.01 N, the value of the E.M.F. is: $0.058/2 \times \log 10/0.01 = 0.029 \times \log 1000 = 0.029 \times 3 = 0.087$ volts.

Determination of Concentrations of Saturated Solutions of Insoluble Substances. Suppose it is desired to ascertain the solubility of silver chloride. A cell is constructed with two silver poles, and deci-normal silver nitrate surrounding one pole, and water containing silver chloride surrounding the other. The silver chloride is so dilute that, as a salt with both radicals univalent, it may be assumed to be practically all ionized. The concentration of the silver ion from this source is found by measuring the E.M.F. of the cell.

Example 53. The observed E.M.F. of the cell is 0.22755 volts. Silver is univalent (0.058/1). In deci-

normal silver nitrate, the concentration of the silver-ion is 0.081. Hence:

$$0.22755 = \frac{0.058}{1} \log \frac{0.081}{x},$$

$$0.22755 = 0.158 \log 0.081 - 0.58 \log x,$$

$$\text{Log } x = \log 0.081 - \frac{0.22755}{0.058} = \bar{2}.90849 - 3.92327,$$

$$\text{Log } x = \bar{6}.98522. \quad \therefore x = 0.00000989.$$

The molar solubility of AgCl given in the table, at 18°, is 0.000009. The calculation, above, ignores the potential difference arising where the two solutions meet, and also ignores the fact that an ionogen, such as potassium chloride, has to be added to the silver chloride solution to render the liquid a good conductor. Hence the divergence between the calculated and observed results.

PROBLEMS.

297. Find the E.M.F. of cells containing normal concentrations of the metal ions, and plates of the corresponding metals: (*a*) Manganese and an acid (with hydrogen electrode), (*b*) zinc and copper, (*c*) zinc and silver. *Ans.* (*a*) 1.04; (*b*) 1.08; (*c*) 1.54.

298. Find the E.M.F. of cells containing, round the active metal pole, normal concentration of the corresponding metal-ion and, round a platinum pole, a halide salt giving normal concentration of the halide-ion and excess of the free halogen: (*a*) Zinc and iodine, (*b*) tin and chlorine, (*c*) copper and bromine. *Ans.* (*a*) 1.28; (*b*) 1.45; (*c*) 0.74.

299. Find the E.M.F. of a cell containing: (*a*) Zinc poles, and 5 *N* Zn^{++} round one pole and 0.001 *N* Zn^{++} round the other, (*b*) tin poles and 2 *N* Sn^{++} round one pole and 0.0001 *N* Sn^{++} round the other. *Ans.* (*a*) 0.1073; (*b*) 0.1249.

300. A cell with silver poles and 0.1 *N* silver nitrate round one pole and silver bromide round the other pole gave an E.M.F. of 0.29756 volts. Calculate the molar solubility of silver bromide. *Ans.* 6×10^{-7}.

301. A cell similar to the above, except that it contained silver iodide, gave an E.M.F. of 0.40069 volts. Calculate the molar solubility of silver iodide. *Ans.* 1×10^{-8}.

302. A cell, with zinc poles, contained 0.1 *N* zinc sulphate (ionized 40 per cent) round one pole and zinc fluoride (insol.) round the other pole. The cell gave an E.M.F. of 0.05519 volts. Calculate the molar solubility of zinc fluoride. *Ans.* 2.475×10^{-4}.

Example 54. If the electrode potential of magnesium is 1.3 volts, when in contact with magnesium chloride solution containing normal magnesium-ion, what would be the theoretical osmotic pressure of magnesium-ion necessary to cut the potential down to 0 volts at 18°?

$$\text{E.M.F.} = \frac{RT}{v} \log \frac{C_1}{C_2}. \quad \text{But } \frac{C_1}{C_2} = \frac{\text{Os. press. } (x)}{\text{Os. press. } N \text{ concn.}}$$

$$1.3 = \frac{0.058}{2} (\log x - \log 11.2 \text{ atmos.}).$$

$$0.029 \log x = 1.3 - 0.029 \log 11.2$$

$$\log x = 44.8 - 1.04922 = 43.75$$

$$x = 10^{43.75} \text{ atmospheres.}$$

Example 55. What is the electrode potential of iron (solution pressure 1.2×10^4 atmospheres) in a solution containing 0.001 molar ferrous-ion?

$$\text{E.M.F.} = \frac{0.058}{v} \log \frac{P}{p},$$

where P is the solution pressure of metallic iron in atmos. and p is the osmotic pressure of the ferrous-ion in atmos. One mole per liter gives 22.4 atmos., hence 0.001 moles give 0.0224 atmos.

$$\text{E.M.F.} = \frac{0.058}{2} \log \frac{1.2 \times 10^4}{0.0224}$$

$$= 0.029 (\log 12{,}000 - \log 0.0224)$$

$$= 0.166 \text{ volts.}$$

PROBLEMS.

303. If the electrode potential of potassium is 3.206 volts when in contact with potassium chloride containing normal potassium-ion, what would be the theoretical osmotic pressure of potassium-ion necessary to cut the potential down to 0 volts at 18° C.? *Ans.* $10^{53.92}$ atmos.

304. Zinc in molar zinc-ion solution has an electrode potential of 0.5 volts. What is the concentration of zinc-ion in equilibrium with zinc at 18° C.? *Ans.* $10^{15.65}$ atmos.

305. What is the electrode potential of cadmium (solution pressure 2.7×10^6 atmos.) in a solution containing 0.01 molar cadmium-ion? *Ans.* 0.205 volts.

306. What is the electromotive force at 18° of a cell containing, in one compartment, cobalt in molar cobalt-ion, in the other iron in molar ferrous-ion, the solutions connected by saturated potassium chloride? *Ans.* 0.15 volts.

PROBLEMS ON OXIDATION AND REDUCTION.

307. Applying formula $E = \frac{0.058}{v} \log \frac{C_{Fe^{+++}}}{C_{Fe^{++}}}$, calculate the electromotive force expressing the tendency of ferric-ion to become ferrous, if we have equimolar solutions mixed, and equilibrium is reached when $C_{Fe^{++}} = 10^{17}\ C_{Fe^{+++}}$. *Ans.* 0.986 volts.

308. Why do not $FeCl_3$ solutions spontaneously become $FeCl_2$ and Cl_2, if the above is correct? Base your answer on the fact that the equilibrium constant for the reaction $\frac{(Cl^-)^2}{Cl_2} = 2 \times 10^{60}$, and calculate the condition of equilibrium for the action: $2Fe^{++} + Cl_2 \rightleftarrows 2Fe^{+++} + 2Cl^-$. *Ans.* $\frac{1}{2 \times 10^{26}}$.

309. The constant K for the equilibrium $\frac{[I^{-2}]}{[I_2]} = 5.6 \times 10^{29}$. Calculate the condition of equilibrium for chlorine to set iodine free from potassium iodide. *Ans.* 2.8×10^{-31}.

310. Calculate the equilibrium relation for the action of ferric salts, iodide ion, ferrous salts and iodine. From these figures arrange the three substances, iodine, ferric-ion, and chlorine in the relative order of their oxidizing power. *Ans.* 5.6×10^{-5}; order: iodine, ferric-ion, chlorine.

311. The solution tension constant of zinc is 1.4×10^{17} moles; for copper it is 8.3×10^{-22}. Calculate the condition of equilibrium between zinc, zinc-ions, copper and copper-ions, and show under what circumstances the reaction may proceed in such a way that *zinc* is precipitated from a zinc solution by metallic copper.

Ans. Equil. const. $\frac{1.4 \times 10^{17}}{8.3 \times 10^{-22}} = 1.7 \times 10^{38}$. If in any way this relation becomes *greater* than 1.7×10^{38}, zinc will be precipitated and copper will go into solution.

CHAPTER X.

THERMOMETRY AND THERMOCHEMISTRY.

Problems in Conversion. 312. Convert 86° F. to Centigrade scale (p. 2). Convert 42° C. to Fahrenheit scale.

Thermochemistry. The heat produced or absorbed in a chemical reaction is conveniently expressed by means of an equation:

$$C + O_2 \rightarrow CO_2 + 97{,}600 \text{ cal.}$$

The unit of heat is the calorie, and is the amount of heat required to raise 1 g. of water 1° at 15°. When heat is absorbed the heat is negative, or may be placed on the other side of the equation:

$$HgO \rightarrow Hg + O - 30{,}600 \text{ cal. or } HgO + 30{,}600 \text{ cal.} \rightarrow Hg + O.$$

The unit of material is one atomic weight, unless the reaction (as in the case of CO_2) requires more than one atomic weight. Molecular equations, like $2H_2 + O_2 \rightarrow 2H_2O$, are not employed in this connection. 1000 cal. = 1 Cal.

Law of Constant Heat Summation (Hess's Law). Very frequently, a substance cannot be prepared from the elements. But, in such a case, several reactions can be used, the choice being made so that the terms not wanted in the final equation cancel out, and so the value for a reaction not itself measurable can be obtained.

Example 56. At 17°, the heat of combustion of carbon to carbon dioxide is 97,000 cal., and that of carbon monoxide (CO) to carbon dioxide is 67,960 cal. (both at constant

gaseous volume, see below). What is the heat of formation of carbon monoxide at constant volume?

$$C + O_2 \rightarrow CO_2 + 97{,}000 \text{ cal.}$$
$$CO_2 \rightarrow CO + O - 67{,}960 \text{ cal.}$$

The second equation must be transposed, so that the CO_2 and O may be canceled:

$$C + O_2 \rightarrow CO_2 + 97{,}000 \text{ cal.}$$
$$CO_2 \rightarrow CO + O - 67{,}960 \text{ cal.}$$

Adding, $C + O \rightarrow CO + 29{,}040$ cal.

Constant Volume and Constant Pressure. When the whole system is kept at constant volume during the reaction, no external work is done. If, however, the reaction is carried out at atmospheric pressure, then, if more gaseous molecules are produced, work is done in expanding the system. Conversely, if fewer gaseous molecules result, work is done by the atmosphere in reducing the volume. In the formation or disappearance of one gram-molecule of gas, the work done is $2T$ calories, where T is the absolute temperature. Thus, if Q is the heat of reaction: Q const. vol. $= Q$ const. press. $+ 2nT$ cal., where n is the number of gram-molecules of gas in excess of that existing before the reaction.

Example 57. Thus, in the case of carbon monoxide, mentioned above, $O = 0.5 \times 22.4$ liters and $CO = 22.4$ liters. At constant pressure, therefore, there is an increase of 0.5×22.4 liters. At constant pressure, therefore, there is here a loss of $2 \times 1/2T = 273 + 17 = 290$ cal., and the value at constant pressure is $29{,}040 - 290$ cal. $= 28{,}750$ cal.

Thermometer. A thermometer is graduated when the whole column of mercury is immersed in the heated

vessel. When a small vessel is used, and part of the column is not heated, the reading is too low, because part of the mercury is not heated and does not expand. The correction is applied as follows: $R = nA\ (t_1 - t_2)$, when n is the number of degrees on the thermometer projecting above the bath, A is the apparent coefficient of expansion of mercury in glass ($A = 0.000157$), t_1 is the temperature shown on the thermometer, and t_2 is the reading on an auxiliary thermometer half way up the exposed thread of mercury. The value of R is to be added to the reading.

PROBLEMS.

313. Calculate the true temperature of a bath when the thermometer in it reads 189° C. and the thread projects from the bath for 124°, the auxiliary thermometer reading 33°. *Ans.* 192°.

314. Guntelberg (Chem. Abs., **10** (1916), 1463) shows that the reaction $NaI + 2H_2O + KClO_3 \rightarrow NaClO_3 + KI + 2H_2O$ occurs at 29.8° C. If the equation $A = 2RT \log_e \frac{p\ (\text{soln.})}{p\ H_2O}$ holds good where A = heat of reaction = -1170 cal. and p soln. and $p\ H_2O$ represent the vapor pressure of the above solution in equilibrium and of water (31.2 mm.), respectively, and $R = 2.0$ cal., calculate the vapor pressure of the system at 29.8°. *Ans.* 11.87 mm.

315. Calculate the heat of formation of sodium molybdate from sodium oxide, oxygen and molybdenum dioxide, if in burning to sodium peroxide, sodium oxide yields 19.4 Cal. and when molybdenum dioxide unites with sodium peroxide, 101.2 Cal. are obtained. *Ans.* 120.6 cal.

316. From the data in **315,** above, calculate how much heat is set free when 5 g. of sodium oxide are oxidized to sodium peroxide. *Ans.* 1.56 Cal.

317. V. Wartenberg (Z. Phys. Chem., **67,** 446) gives the following values for the heats of formation of cuprous sulphide, 18.97 ± 0.06 Cal. for the reactions:

$$2Cu + S_{rh} = Cu_2S + 18.97 \pm 0.06\ \text{Cal.}$$
$$2Cu + S_{\mu} = Cu_2S + 19.69 \pm 0.13\ \text{Cal.}$$

Calculate the heat of formation of S_μ from S_{rh}. *Ans.* 0.72 $\pm$ 0.19 Cal.

318. In the article referred to in **317,** above, it is stated that $2Cu + 2S_{rh} = 2CuS + 23.22 \pm 0.11$ Cal. Calculate the heat set free when $Cu_2S + S_{rh}$ unite to form 2CuS. *Ans.* 4.25 $\pm$ 0.16 Cal.

319. If the heat of combustion of cane sugar is 16.545 kilojoules per gram (1 kilojoule = 239.1 Cal.), what is its molar heat of combustion in Calories? *Ans.* 1347.2 Cal.

320. From the heat of fusion for antimony tribromide, $SbBr_3$ (9.76 cal. for 1 g.), and its melting-point 94.2° C., calculate K, the molar depression of its freezing-point for one gram-molecule in 100 g. of solvent, using the formula, $K = \frac{0.02\ T^2}{q}$, where T is the freezing-point in degrees absolute and q is the latent heat of fusion of 1 g. in small calories. How is the above formula derived (see Walker's Introduction to Physical Chemistry)? *Ans.* 270.13°.

321. A mercury-in-glass thermometer is calibrated at 0° C.; 32.4°; at the boiling-point of water (barometer = 752 mm.); and at the freezing-point of tin (232° C.). At 0° the reading is +0.5°; at 32.4° (transition point of sodium sulphate decahydrate) 33.1°, at the boiling-point of water 98.5° C., and at the melting-point of tin 226°. In the latter case 105° of mercury are out of the freezing metal, while the auxiliary thermometer half way up the stem read 61°. Assuming the errors in the above thermometer are equally distributed between any two adjacent calibration points, what would be the true temperatures when this thermometer indicates 15°, 57°, 134°, and 212°, assuming complete immersion in the baths at the temperatures given? *Ans.* 14.4°; 57°; 136.3°; 216°.

322. In using the thermometer in **321,** above, the uncorrected melting-point of an organic compound was found to be 204° C.; and 154° C. were out of the bath. The auxiliary temperature, half way up the emergent column, was 43°. What was the true melting-point of the compound? *Ans.* 210.3°.

323. A certain thermocouple developed an electromotive force of 4.74 millivolts when the hot junction was at 100° C. and the cold junction was at 24° C. When the cold junction was at 24° and the hot junction at 150°, the electromotive force was 7.75 m.v. What would be the reading if the hot junction was at 122° C., and the cold junction as above, assuming the relation between temperature dif-

ferences and E.M.F. to be linear within this region? *Ans.* 6.06 millivolts.

324. If the molar heat of combustion of benzol is 3278 kilojoules (1 kilojoule = 239.1 Cal.), what would be the final temperature in a calorimeter having a water equivalent of 3500, if 0.542 g. of benzol are burned in it, the original temperature being 24.0° C.? (See Richards & Jesse, Jour. Am. Chem. Soc., **32** (1910), 289.) *Ans.* 25.556°.

325. If K, the freezing constant for naphthalene, is 68.99, what is its latent heat of fusion? (Freezing-point of naphthalene is 79.25° C. See problem **320,** above.) *Ans.* 35.97 calories.

326. How much ice at 0° C. would be melted (heat of fusion per gram 79 cal.), if 10 g. of naphthalene (sp. ht. 0.325 cal.; ht. of fusion, 35.97 cal. per 1 g.), just at its freezing-point (79.25°), is dropped upon a large ice sheet? *Ans.* 9.04 g.

CHAPTER XI.

REACTION RATES AND ORDER OF REACTIONS.

Reaction Rates. At a constant temperature, the rate at which a reaction proceeds depends upon the affinity or tendency to interaction, and upon the concentration of the substance (or substances) being transformed [291–297, *181–184*]. The affinity is constant, but as the material is gradually transformed, its concentration diminishes, and so the rate of the reaction becomes slower and slower. The rate at constant concentration, however, can be calculated from the observations.

Monomolecular Reactions. For a reaction in which interaction between molecules does not occur, or in which one interacting substance remains constant in concentration, because it is present in great excess, the inversion of sugar in presence of an acid (unchanged) may be taken as an example.

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

Here the water is in great excess, and so only the sugar molecules diminish in concentration. The measurement is made by observing the change in the angle of rotation of the plane of polarization of light passing through the solution. Thus, in one series, the change in rotation when the action was complete, was 65.5°. The rate recorded in degrees was:

Time, mins.	x.	Time, mins.	x.
0	....	150	24.75
30	5.75°	330	44.00
60	11.00	630	56.75
90	16.00	∞	65.50

The formula $\frac{1}{t} \log_e \frac{a}{a-x}$ = constant gives the speed with unit concentration, if the latter could be maintained unchanged during the whole period. a is the total, x the amount transformed, and t the time in minutes.

Example 58. For 30 minutes $\frac{1}{30} \log_e \frac{65.5}{65.5 - 5.75} = 0.00306$.

PROBLEM.

327. Find the constant for sugar at 90 minutes, at 330 minutes, and at 630 minutes. *Ans.* 0.0034, 0.00337, 0.00319.

Dimolecular Reactions. When *two* substances diminish in concentration during the action, a different formula is used. $\frac{1}{t} \frac{x}{a(a-x)}$ = constant. For such a reaction, the formula for a monomolecular reaction gives inconstant values. Thus, the decomposition of ethyl acetate by an equivalent of sodium hydroxide:

$$C_2H_5.COOCH_3 + NaOH \rightarrow C_2H_5OH + NaCOOCH_3.$$

By titration with an acid, the diminishing concentration of sodium hydroxide, and therefore the progress of the reaction, can be measured. In the following data, 16 c.c. of hydrochloric acid was required to neutralize the whole of the sodium hydroxide. Hence x, representing the

amount of the two substances used up, is equal to 16 minus the amount of acid still required.

Time, mins.	x.	Time, mins.	x.
5	5.76	35	12.59
15	9.87	55	13.69
25	11.68	120	14.90

Example 59. $\frac{1}{t}\frac{x}{a\,(a-x)} = \frac{1}{5}\frac{5.76}{16(16-5.76)} = 0.00703.$

PROBLEM.

328. Find the values of the constant at 25 minutes, and at 55 minutes. *Ans.* 0.0067, 0.0067.

Finding the Order of a Reaction. The order of a reaction cannot be judged by merely examining the equation. Thus, in the oxidation of hydriodic acid by hydrogen peroxide: $H_2O_2 + 2HI \rightarrow 2H_2O + I_2$, one would suppose that three molecules were interacting, and that therefore the reaction was termolecular. In fact, however, the reaction proceeds in two stages: $HI + H_2O_2 \rightarrow HIO + H_2O$, and $HI + HIO \rightarrow H_2O + I_2$, and of these only the first goes slowly enough to be measured. Hence the reaction fits the dimolecular equation. To determine the order of a reaction, therefore, one must try both formulæ and find out which gives constant values.

PROBLEMS.

329. Sodium hydroxide acts upon sodium chloracetate to give sodium glycolate and sodium chloride: $NaCOOCH_2Cl + NaOH \rightarrow NaCOOCH_2OH + NaCl$. Find the order of the reaction, where $a = 14.90$:

Time, mins.	x.	Time, mins.	x.
9	0.80	149	6.90
29	2.15	254	8.85
119	5.95	∞	14.90

Ans. Dimolecular.

330. Methyl acetate is decomposed by excess of water in presence of an acid: $CH_3COOCH_3 + H_2O \rightarrow CH_3COOH + CH_3OH$. When complete, neutralization of the acetic acid formed requires 14.11 c.c. of barium hydroxide solution:

Time, mins.	x.	Time, mins.	x.
14	0.92	159	7.59
34	2.14	239	9.77
59	3.52	∞	14.11

Find the order of the reaction. *Ans.* Monomolecular.

331. Wibant (Chem. Abstracts, **10** (1916), 184) gives the following data on the velocity at 25° C. of nitration of benzene in acetic anhydride: Initial conc. of C_6H_6, $0.5N$; for the times noted below, the following nitric acid concentrations:

Time, mins.	0	44	102	221	347	433	558
C.	0.7174	0.6837	0.6505	0.5879	0.5331	0.4972	0.4336

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O.$$

Calculate the velocity constant, using the dimolecular formula. *Ans.* Av. = 0.00255.

332. Malemgrean and Prigent (Z. Physiol. Chem., **73,** 68) state that the hydrolysis of glycerophosphoric acid $C_3H_5(OH)_2,H_2PO_4$ is monomolecular. Calculate the amount of free phosphoric acid formed after two hours, if in a tenth normal solution. $K = 0.01025$ at 100° C. *Ans.* 4.611 g. = 0.047 moles per liter.

333. Mercuric acetate and anilin react, forming acetic acid and a complex organic mercury base. If at 25° the velocity constant is 0.000841, calculate the time necessary to set free half the theoretical amount of acetic acid from a solution, containing the above constituents in 0.1 molar concentration, using the dimolecular formula. *Ans.* 99 hours 5 minutes.

CHAPTER XII.

CURVE PLOTTING.

In plotting curves, use paper ruled with lines 1 mm. apart. The rulings are vertical as well as horizontal, so that the paper is divided into squares 1 mm. by 1 mm. A heavier line is used for lines 10 mm. apart.

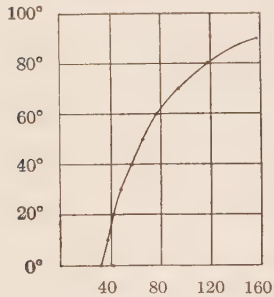

Fig. 2

Example 60. Plot the solubilities of hydrated cupric sulphate $CuSO_4,5H_2O$. The temperatures are plotted vertically, starting at 0° near the foot of the paper. The solubilities are plotted to the right. The following figures give the temperatures, and the corresponding weights of $CuSO_4$ per 100 c.c. of water (Fig. 2).

Temp.	0°	10°	20°	30°	40°
g. per 100 c.c.	31.61	36.95	42.31	48.81	56.90
Temp.	50°	60°	70°	80°	90°
g. per 100 c.c.	65.83	77.39	94.60	118.03	156.44

Sometimes, as in problem **334,** the weight of the substance in 100 g. of the solution is given. In this case, the amount of water is ascertained by subtracting the weight of the substance from 100 g. of solution.

Example 61. Plot the temperature vertically and the molecular per cent of acid to the right, starting with 100

per cent. Mixtures of anisaldehyde and trichloracetic acid give the following freezing-points (Fig. 3):

Per cent acid	100	80.9	69.8	67.6	61.8	55.3	48.7
T	57.9	37.7	14.5	17.9	24.4	29.4	30.7
Per cent acid	41.8	35.1	27.1	18.8	12.0	6.8	0
T	27.7	21.9	12.6	0.3	−8.1	−4.9	−0.9

The maximum in the curve at 50 per cent indicates an equimolecular compound. The freezing-points are lower on each side because excess of either substance lowers the freezing-point.

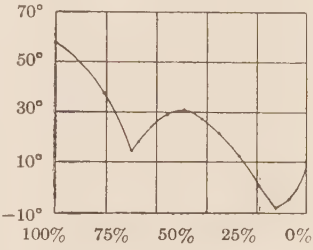

Fig. 3

PROBLEMS.

334. Plot solubility of boric acid in water against temperature from the following data. Sol. equals g. H_3BO_3 in 100 g. solution:

Temp., degs. C.	Soln.	Temp., degs. C.	Soln.
0	2.59	69.5	15.58
12.2	3.69	80.0	19.11
21.6	4.90	90.0	23.30
31.0	6.44	99.5	28.10
40.0	8.02	108.0	36.70
50.0	10.35	115.0	45.00
60.0	12.90	120.0	52.40

(Nasini & Ageno, Z. Phys. Chem., **69,** 482–5.) Solid changes to HBO_2 at 108°.

335. From data in **241,** Chap. VII, plot the change with temperature of conductivity and of dissociation of 0.25 *M* sodium thiocyanate.

336. Kendall & Gibbons (Jour. Am. Chem. Soc., **37** (1915), 149) obtained the following melting-points when acetophenone was added to trichloracetic acid:

Per cent acid.	M.-p.	Per cent acid.	M.-p.
100	57.3	43.0	23.3
91.4	50.5	36.5	18.1
83.8	41.9	30.7	11.6
72.0	21.3	25.1	3.7
63.8	−2.2; 17.9	19.9	5.1
58.3	22.9	14.5	10.1
52.1	25.6	8.4	14.4
48.4	25.7	0.0	18.7

Plot the curve, and interpret results.

337. A 50 c.c. burette was calibrated and yielded these results:

Burette reading.	Actual water del.	Burette reading.	Actual water del.
c.c.		c.c.	
5.00	4.98	30.00	29.90
10.00	9.93	35.00	34.89
15.00	15.00	40.00	39.93
20.00	20.07	45.00	44.91
25.00	25.01	50.00	49.99

Plot results: (*a*) showing actual water delivered against burette reading; and (*b*) *error* against burette reading.

338. A base metal thermocouple was calibrated (cold junction at 24° C.), with the following results in millivolts:

Temp., degs.	Mvs.	Temp., degs.	Mvs.
24	0	400	28.83
100	4.77	450	32.70
150	8.82	500	36.63
200	12.95	550	40.50
250	17.02	600	44.23
300	21.00	650	48.11
350	24.96	.....	.....

A scale was now made for the direct reading millivoltmeter on the above basis. Six months after it was made, this meter was recalibrated, the *scale* readings then being found to correspond to the following E.M.F.'s in millivolts:

Temp., degs.	Mvs.	Temp., degs.	Mvs.
24	0	400	28.71
100	4.82	450	32.61
150	8.80	500	36.63
200	12.95	550	40.80
250	17.07	600	44.20
300	20.90	650	48.17
350	24.91	.....	.....

On the assumption that the couple had not changed, plot a curve showing *true temperatures* against the scale readings of the *new* calibration.

339. Hall & Harkins (Jour. Am. Chem. Soc., **38** (1916) 2658) give the following results on freezing-points of erythrite solutions in water:

Conc., $N\times10^3$.	F.-p. depression, degs. C.	Conc.	F.-p. depression, degs. C.
1.85	0.00338	62.84	0.1171
4.83	0.00883	127.14	0.2375
10.57	0.01958	335.5	0.6304
23.00	0.04273	652.4	1.2371

Devise a means of plotting these results on a small scale, and plot.

340. The following figures show part of the solubility value of $As_2O_5,4H_2O$ and $3As_2O_5,5H_2O$ (Menzies and Potter, Jour. Am. Chem. Soc., **34** (1912), 1452). Plot these solubilities against temperature and interpret the result. Solubility, parts of H_3AsO_4 in 100 parts of solution.

Temp., degs. C.	$As_2O_5,4H_2O$.	$3As_2O_5,5H_2O$.	Temp., degs. C.	$As_2O_5,4H_2O$.	$3As_2O_5,5H_2O$.
5	82.1	.....	30	90.0	89.8
10	83.3	88.4	35	92.8	.....
15	84.7	.....	40	.....	90.5
20	86.3	89.1	50	.....	91.2
25	88.0	.....	.....	.....	.....

341. Plot the clean-up of oxygen in a tungsten lamp from the following figures given by Langmuir (Jour. Am. Chem. Soc., **35** (1913), 105).

Time, mins.	Cubic mm. oxygen.	Time, mins.	Cubic mm. oxygen.
0	14.09	11	1.66
1	10.58	13	1.05
3	7.59	17	0.40
5	5.42	20	0.25
7	3.20	23	0.18
9	2.50	.....	.....

342. Lenher & Wolesensky (Jour. Am. Chem. Soc., **35** (1913), 718) dehydrated magnesium tellurite, $MgTeO_3,5H_2O$ at different temperatures, with the following results:

Temp., degs. C.	H_2O held by 1 g. $MgTeO_3$.	Temp., degs. C.	H_2O held by 1 g. $MgTeO_3$.
20	0.1545	260	0.0758
100	0.1360	300	0.0250
130	0.1170	330	0.0130
175	0.0965	360	0.0080
200	0.0869	400	0.0050
220	0.0838	450	0.0000

Plot and interpret.

343. Read the article by Jackson on Equilibrium in the System: Lead acetate, lead oxide, and water, at 25°; plot the results and interpret the figure. (Jour. Am. Chem. Soc., **36** (1914), 2346.)

344. Neumann and Bergve give (Zeit. Electrochemie, **21** (1915), 143) the following values in volts for the decomposition potentials (π) of fused sodium and potassium hydroxides:

Temp., degs. C.	π NaOH, volts.	Temp., degs. C.	π NaOH, volts.	Temp., degs. C.	π KOH, volts.
180	2.38	335	2.22	200	2.4
200	2.32	390	2.05	230	2.37
230	2.29	450	1.87	280	2.34
280	2.25	530	1.52	305	2.36
305	2.25	640	1.32	335	2.40
.....	.....	.....	.....	380	2.25
.....	.....	.....	.....	530	1.80

Plot results and interpret.

345. Askenasy & Klonowski (Zeit. Electrochemie, **16,** 104–114) state that the dissociation pressure of manganese dioxide ($2MnO_2 = Mn_2O_3 + 1/2O_2$) has the following values at the temperatures shown:

Temp., Degs. C.	382	448	478	536
Pressure (mm.).	23	125	200	71040

They also give the dissociation pressure of potassium permanganate ($K_2MnO_4 = K_2MnO_3 + 1/2O_2$) as follows:

Temp., Degs. C.	410	454	548	586	616	652	668
Pressure (mm.).	2	5	40	109	235.5	568	763

Plot and interpret.

346. C. & M. Cuthbertson (Proc. Roy. Soc. London (A), **85,** 306) give the following formula for the vapor pressure of bromine from $-80°$ C. to $-7°$ C. $P = ab^T$, where $a = 2.485 \times 10^{-8}$ and $b = 1.0834$. Plot the curve of above equation (T = temp. in degrees absolute).

347. Plot the surface tension in dynes per sq. centimeter of water for every 5° C. from 0° C. to 75° C. from the following formula (Morgan & McAfee, Jour. Am. Chem. Soc., **33** (1911), 1275), $Yt = 75.872 - 0.1547\,t - 0.000222\,t^2$, where t is the temperature in centigrade degrees.

348. Plot the ratio cp/cv for ether at 60° C. for the following pressures (in atmospheres) (Lussarea, Chem. Abs., **8** (1910), 3738):

cp/cv	1.329	1.298	1.178	1.144	1.139
P	94.000	143.000	500.000	863.000	954.000

Interpret.

349. Plot the change with concentration of osmotic pressure of cane sugar solutions, at 20° C., from the following data given by H. N. Morse and his collaborators:

Conc. moles per l.	Os. pressure (atm.)	Conc. moles per l.	Os. pressure (atm.).
0.1	2.590	0.6	15.388
0.2	5.064	0.7	18.128
0.3	7.605	0.8	20.905
0.4	10.137	0.9	23.717
0.5	12.748	1.0	26.638

350. Plot the change with temperature of osmotic pressure of cane sugar solutions from the following data for 0.5 molar solution:

Temp., Degs. C.	0	5	10	15	20	25
Os. press. (atm.).	11.895	12.100	12.297	12.549	12.748	12.943

APPENDIX.

I. Densities of Water (1 c.c. at 4° = 1 g.).

−10°	0.998	25°	0.997	65°	0.981
−5	0.999	30	0.996	70	0.978
0	0.9999	35	0.994	75	0.975
4	1.000	40	0.992	80	0.972
5	0.99999	45	0.990	85	0.969
10	0.9997	50	0.988	90	0.9655
15	0.999	55	0.986	95	0.962
20	0.998	60	0.983	100	0.9587

II. Vapor Pressures of Water.

Both the Fahrenheit (F.) or ordinary and the Centigrade (C.) temperatures are given.

Temperature.		Pressure, mm.	Temperature.		Pressure, mm.
F.	C.		F.	C.	
32°	0°	4.6	71.6°	22°	19.7
41	5	6.5	73.4	23	20.9
46.4	8	8.0	75.2	24	22.2
48.2	9	8.6	77.0	25	23.6
50.0	10	9.2	78.8	26	25.1
51.8	11	9.8	80.6	27	26.5
53.6	12	10.5	82.4	28	28.1
55.4	13	11.2	84.2	29	29.8
57.2	14	11.9	86.0	30	31.5
59.0	15	12.7	87.8	31	33.4
60.8	16	13.5	89.6	32	35.4
62.6	17	14.4	91.4	33	37.4
64.4	18	15.4	93.2	34	39.6
66.2	19	16.3	95.0	35	41.8
68.0	20	17.4	.....	.....	.....
69.8	21	18.5	212.0	100	760.0

III. Correction of Barometer (Glass) to 0° C.

Subtract number from reading.

Temp.	Barometric reading (mm.).				
	730	740	750	760	770
7°	0.89	0.91	0.92	0.93	0.94
8	1.01	1.03	1.04	1.05	1.07
9	1.14	1.16	1.17	1.19	1.20
10	1.27	1.29	1.30	1.32	1.34
11	1.40	1.42	1.44	1.45	1.47
12	1.53	1.55	1.57	1.59	1.61
13	1.65	1.67	1.69	1.71	1.73
14	1.78	1.80	1.82	1.84	1.87
15	1.90	1.93	1.95	1.98	2.00
16	2.03	2.06	2.09	2.11	2.14
17	2.16	2.19	2.22	2.24	2.26
18	2.28	2.31	2.34	2.37	2.40
19	2.41	2.44	2.47	2.50	2.53
20	2.54	2.57	2.60	2.63	2.67
21	2.67	2.70	2.73	2.77	2.80
22	2.79	2.83	2.87	2.90	2.94
23	2.91	2.95	2.99	3.02	3.06
24	3.04	3.08	3.12	3.16	3.20
25	3.17	3.21	3.25	3.29	3.33
26	3.30	3.34	3.37	3.42	3.47
27	3.42	3.47	3.51	3.56	3.60
28	3.54	3.59	3.63	3.68	3.73
29	3.67	3.72	3.77	3.81	3.86
30	3.80	3.85	3.90	3.95	3.99

IV. International Atomic Weights (1918).

		O=16.
Aluminium	Al	27.1
Antimony	Sb	120.2
Argon	A	39.88
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.92
Cadmium	Cd	112.40
Caesium	Cs	132.81
Calcium	Ca	40.07
Carbon	C	12.005
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.1
Copper	Cu	63.57
Dysprosium	Dy	162.5
Erbium	Er	167.7
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	69.9
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	4.00
Holmium	Ho	163.5
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron	Fe	55.84
Krypton	Kr	82.92
Lanthanum	La	139.0
Lead	Pb	207.20
Lithium	Li	6.94
Lutecium	Lu	175.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.6
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.2
Nickel	Ni	58.68
Niton (radium emanation)	Nt	222.4
Nitrogen	N	14.01
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Praseodymium	Pr	140.9
Radium	Ra	226.0
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	44.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulphur	S	32.06
Tantalum	Ta	181.5
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.4
Thulium	Tm	168.5
Tin	Sn	118.7
Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	238.2
Vanadium	V	51.0
Xenon	Xe	130.2
Ytterbium (Neoytterbium)	Yb	173.5
Yttrium	Yt	88.7
Zinc	Zn	65.37
Zirconium	Zr	90.6

V. Ionization Constants of Acids and Bases.

Acids		
Nitrous		5.0×10^{-4}
Hydrocyanic		7.2×10^{-10}
Carbonic	$H^+ \times HCO_3^-/H_2CO_3$	5×10^{-7}
	$H^+ \times CO_3^=/HCO_3^-$	7×10^{-11}
Acetic		1.8×10^{-5}
Phosphoric	$H^+ \times H_2PO_4^-/H_3PO_4$	1.0×10^{-2}
	$H^+ \times HPO_4^=/H_2PO_4^-$	2.0×10^{-7}
	$H^+ \times PO_4^=/HPO_4^=$	4.0×10^{-13}
Oxalic	$H^+ \times HC_2O_4^-/H_2C_2O_4$	3.8×10^{-2}
	$H^+ \times C_2O_4^=/HC_2O_4^-$	5.0×10^{-5}
Bases		
Potassium hydroxide		1
Sodium hydroxide		1
Ammonium hydroxide		1.8×10^{-5}

VI. Sensitiveness of Indicators.

Indicator with acids.	Color change.	Concn. H^+.
Phenolphthalein	Pink → colorless	1×10^{-9}
Azolitmin (litmus)	Violet → violet-pink	1×10^{-7}
Methyl-orange	Yellow → red-orange	$1 \times 10^{-4} - 1 \times 10^{-5}$

Indicator with bases.	Color change.	Concn. OH^-
Phenolphthalein	Colorless → pink	1×10^{-6}
Azolitmin	Violet → violet-blue	$1 \times 10^{-7} - 1 \times 10^{-8}$
Methyl-orange	Orange → yellow	1×10^{-10}

VII. Diagram of Solubilities.

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